Rongalite as a mild reductant for solvent-assisted dechlorination of 3,3-dichlorooxindoles to 3-chloro-2-oxindoles and 2-oxindoles

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1. General information

All chemicals and solvents were purchased from Alfa Aesar, Spectrochem, SRL, Finar and used as received. Thin layer chromatography was performed on 200 µm aluminium-foil backed silica gel plates and the column chromatography was performed using 100-200 mesh silica gel (Merk). ^{1}H NMR spectra were recorded on Bruker Avance 400 MHz spectrometer, $CDCl_3$ and DMSO-d_6 as solvents, and TMS as an internal standard. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Coupling constants, *J* were reported in Hertz unit (Hz). ^{13}C NMR spectra were recorded on Bruker Avance 100 MHz spectrometer, and they were fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.16 ppm of chloroform-*d* (a multiplet at 39.52 ppm of DMSO-d_6). Melting points were determined with a Stuart SMP30 apparatus, and are uncorrected. FT-IR spectra were recorded on a Perkin Elmer spectrometer. HRMS were analyzed with Agilent Q-TOF 6230.

3,3-Dichlorooxindoles **1** were prepared from literature reports, and rongalite **2** is purchased from SRL.

2. General procedures

General procedure for the synthesis of 3,3-dichloro-2-oxindoles (1a-1r) [1]

An oven-dried 25 mL round-bottom flask equipped with a magnetic stirring bar was charged with the appropriate isatin (10 mmol, 1.0 equiv.) and benzene (10 mL). Phosphorus pentachloride (30 mmol, 3.0 equiv.) was then added portionwise under ambient conditions. The reaction mixture was stirred at room temperature, and the progress was monitored by TLC using hexane/ethyl acetate as the eluent. Upon completion, the reaction mixture was concentrated, and the resulting black residue was purified by column chromatography to afford the corresponding 3,3-dichloroindolin-2-one.

General procedure for the synthesis of 3,3-dibromo-2-oxindoles (5a-5c) [2]

An oven-dried 25 mL round-bottom flask equipped with a magnetic stirring bar was charged with the appropriate 2-oxindole (10 mmol, 1.0 equiv.) and ethyl acetate (10 mL). Copper(II) bromide (30 mmol, 3.0 equiv.) was then added, and the reaction mixture was heated to reflux with continuous stirring. The progress of the reaction was monitored by TLC using hexane/ethyl acetate as the eluent. Upon completion, the reaction mixture was cooled to room temperature, diluted with water (10 mL), and extracted with ethyl acetate (3 × 10 mL). The

combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude residue was purified by column chromatography on silica gel using hexane/ethyl acetate as the eluent to afford the corresponding 3,3-dibromoindolin-2-one.

General procedure (A) for Synthesis of 3-chloroindolin-2-ones (3a- 3r)

An oven dried 10 mL reaction flask equipped with a magnetic stirring bar was charged with 3,3-dichloro-2-oxindole **1** (0.5 mmol), rongalite **2** (1.0 mmol), and EtOH. The mixture was stirred at 70 ºC for 3-5 min. The progress of the reaction was monitored by TLC using hexane, and ethyl acetate as an eluent. After the completion of reaction, water is added to the reaction mixture, and the organic compound is extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried on Na_2SO_4, and evaporated to give a residue that was purified on a short pad of silica gel by column chromatography using hexane, and ethyl acetate as an eluent.

General procedure (B) for Synthesis of indolin-2-ones (4a- 4r)

An oven dried 10 mL reaction flask equipped with a magnetic stirring bar was charged with 3,3-dichloro-2-oxindole **1** (0.5 mmol), rongalite **2** (1.5 mmol), and DMSO. The mixture was stirred at 70 ºC for 5 min. The progress of the reaction was monitored by TLC using hexane, and ethyl acetate as an eluent. After the completion of reaction, water is added to the reaction mixture, and the organic compound is extracted with ethyl acetate (3 x 10 mL). The combined organic layers were dried on Na_2SO_4, and evaporated to give a residue that was purified on a short pad of silica gel by column chromatography using hexane, and ethyl acetate as an eluent.

General Experimental procedure(C) for Synthesis of 3-bromoindolin-2-ones (6a- 6c)

An oven dried 10 mL reaction flask equipped with a magnetic stirring bar was charged with 3,3-dibromoindolin-2-one **1** (0.5mmol), rongalite **2** (1mmol), and EtOH. The mixture was stirred at 80 ºC for 3-5 min. After completion of the reaction, as monitored by the TLC using hexane, and ethyl acetate as an eluent, added 10mL of water and extracted with ethyl acetate (3 X 10 mL). The organic layers were separated dried over Na_2SO_4, and evaporated under reduced pressure to give a residue, was purified on a short pad of silica gel column chromatography by using hexane, and ethyl acetate as an eluent.

Deuterium labeling studies

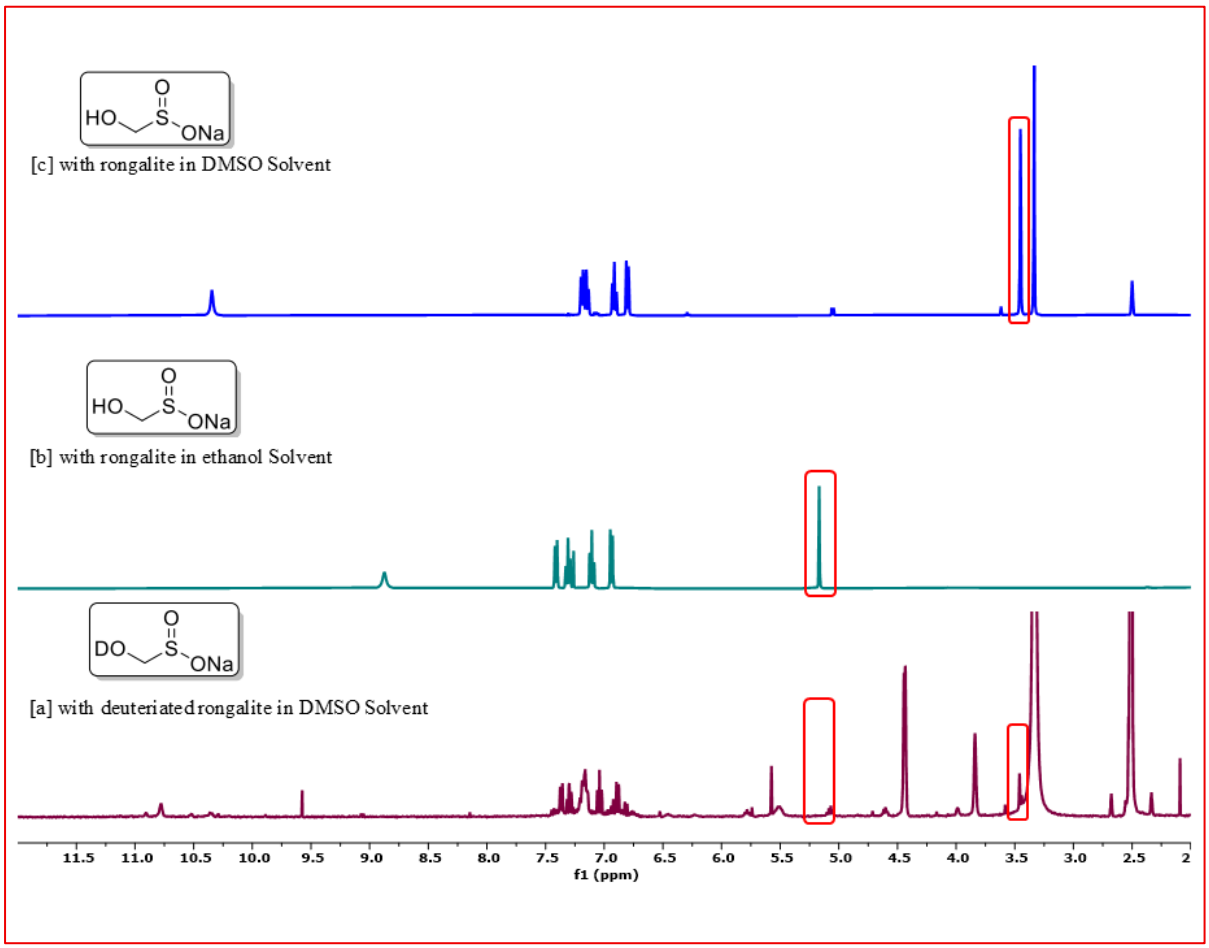
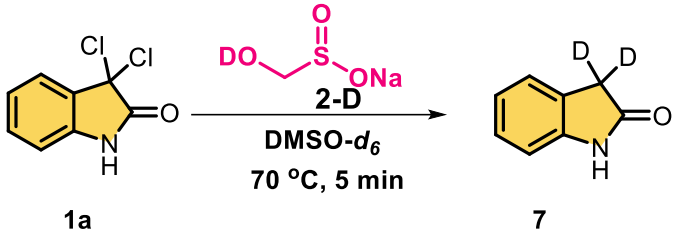


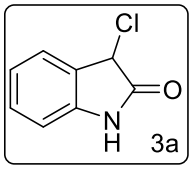
Figure S1. ^{1}H NMR spectra of panel (a) Deuterated rongalite; panel (b) Rongalite in ethanol solvent; panel (c) Rongalite in DMSO solvent.



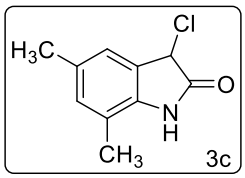
An oven dried 10 mL reaction flask equipped with a magnetic stirring bar was charged with 3,3-dichloro-oxindole **1a** (l.0 equiv), and deuterated rongalite **2**-D (2.5 equiv) in DMSO-d_6 (1 mL) and the mixture was stirred at 70 °C for 5 min under N_2 atmosphere. After 5 min., 10 µL aliquots of the reaction mixture were withdrawn, diluted with DMSO-d6 (0.5 mL), and recorded ^{1}H NMR spectrum. The peaks at δ 5.16 ppm and δ 3.45 ppm disappeared corresponding to product **3a**, and **4a** respectively (Figure S1). Based on ^{1}H NMR data, we have found that deuterium was incorporated in the product **7**. This result suggested that the proton from the rongalite got itself incorporated into the final product.

Characterization data

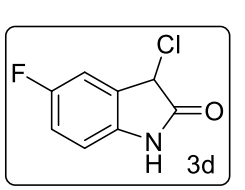
3-chloroindolin-2-one (3a). Off White solid; Yield (73 mg, 89%); mp 136 - 140 °C; The title compound was prepared, according to the general procedure (A) as described above; FT-IR (KBr, cm^{-1}) 3152, 2940, 1743, 1683, 1622, 1470, 776, 741, 682; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.88 (s, 1H), 7.41 (d, J = 7.6 Hz, 1H), 7.31 (t, J = 7.6 Hz, 1H), 7.11 (dt, J = 7.6, 3.8 Hz, 1H), 6.94 (d, J = 7.8 Hz, 1H), 5.17 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ (ppm): 174.76, 141.0, 130.6, 126.3, 126.0, 123.5, 110.7, 52.0; HRMS (ESI) m/z: $[M+H]^+$ calcd for C_8H_7ClNO 168.0216; found 168.0209.



3-chloro-5-methylindolin-2-one (3b). pale red solid; Yield (70 mg, 82%); mp 110 °C; The title compound was prepared, according to the general procedure (A) as described above; FT-IR (KBr, cm^{-1}) 3034, 2923, 1710, 1626, 1492, 813, 686; ^{1}H NMR (400 MHz, $CDCl_3$+DMSO-d_6) δ (ppm): 10.02 (s, 1H), 7.08 (s, 1H), 6.98 – 6.95 (m, 1H), 6.68 (d, J = 8.0 Hz, 1H), 4.98 (s, 1H), 2.22 (s, 3H); ^{13}C{^{1}H} (100 MHz, $CDCl_3$+DMSO-d_6) δ (ppm): 173.9, 139.7, 132.2, 130.7, 126.2, 126.2, 110.3, 52.4, 20.9; HRMS (ESI) m/z: $[M+H]^+$ calcd for C_9H_9ClNO 182.0373; found 182.0364.

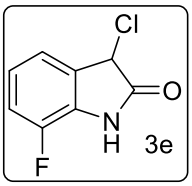


3-chloro-5,7-dimethylindolin-2-one (3c). Off white solid; Yield (60 mg 85%); mp 115 °C; The title compound was prepared, according to the general procedure (A) as described above; FT-IR (KBr, cm^{-1}) 3188, 3084, 2926, 1715, 1627, 1482, 864, 739; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 10.61 (s, 1H), 6.93 (s, 1H), 6.86 (d, J = 0.8 Hz, 1H), 5.45 (s, 1H), 2.16 (s, 3H), 2.09 (s, 3H); ^{13}C{^{1}H} (100 MHz, DMSO-d_6) δ (ppm):173.6, 138.5, 131.9, 131.3, 126.2, 123.5, 119.4, 52.8, 20.5, 16.3; HRMS (ESI) m/z: $[M-H]^-$ calcd for $C_{10}H_{11}ClNO$ 194.0373; found 194.0373.

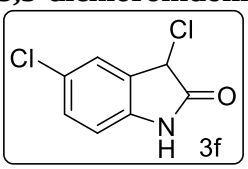


3-chloro-5-fluoroindolin-2-one (3d). Off white solid; Yield (75 mg 89%); mp 179-183 °C; The title compound was prepared, according to the general procedure (A) as described above; FT-IR (KBr, cm^{-1}) 3158, 2936, 1748, 1683, 1488, 1273; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm):10.79 (s, 1H), 7.29 (dd, J = 8.2, 2. Hz, 1H), 7.15 (td, J = 6.8, 0.5 Hz, 1H), 6.88 (dd, J = 8.6, 4.4 Hz, 1H), 5.59 (s, 1H); ^{13}C{^{1}H} (100 MHz, DMSO-d_6) δ (ppm):173.6, 159.8 (d, $^1J_{C\text{-}F}$ = 236.4 Hz), 139.0, 128.6, (d, $^3J_{C\text{-}F}$ = 8.92 Hz), 117.3, (d, $^2J_{C\text{-}F}$ = 23.24 Hz), 113.9, (d, $^2J_{C\text{-}F}$ = 25.03 Hz), 111.6, (d, $^4J_{C\text{-}F}$ = 8.06 Hz), 52.5; HRMS (ESI) m/z: $[M-H]^-$ calcd for C_8H_4ClFNO 183.9965; found 183.9971.

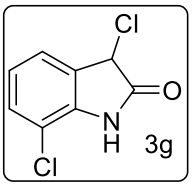
3-chloro-7-fluoroindolin-2-one (3e). Pale red solid; Yield (70 mg 70%); mp 172 °C; The title compound was prepared, according to the general procedure (A) as described above; FT-IR (KBr, cm^{-1}) 3154, 3083, 2818, 1730, 1642, 1497, 1208, 796, 720; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm):11.31 (s, 1H), 7.23 (dd, J = 8.4, 3.8 Hz, 2H), 7.09 – 7.04 (m, 1H), 5.66 (s, 1H).; ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ (ppm):173.4, 147.9, (d, $^{1}J_{C\text{-}F}$ = 241.72 Hz), 130.0, (d, $^{2}J_{C\text{-}F}$ = 29.56 Hz), 129.8, (d, $^{3}J_{C\text{-}F}$ = 3.6 Hz), 123.7, (d, $^{3}J_{C\text{-}F}$ = 5.8 Hz), 122.1, (d, $^{4}J_{C\text{-}F}$ = 2.81 Hz), 117.8, (d, $^{2}J_{C\text{-}F}$ = 17.08 Hz),52.4, 52.3; HRMS (ESI) *m/z*: [M-H]$^{-}$ calcd for C_8H_4ClFNO 183.9965; found 183.9971.



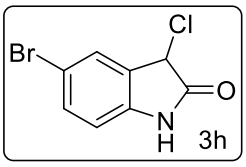
3,5-dichloroindolin-2-one (3f). Off white solid; Yield (55 mg, 64%) mp 199-202 °C ; The title compound was prepared, according to the general procedure (A) as described above; FT-IR (KBr, cm^{-1}) 3178, 2932, 1747, 1685, 1621, 1476, 827; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm):10.95 (s, 1H), 7.50 (d, J = 2.0 Hz, 1H), 7.42 (dd, J = 8.0, 2.8 Hz, 1H), 6.95 (d, J = 8.4 Hz, 1H), 5.65 (s, 1H); ^{13}C{^{1}H} (100 MHz DMSO-d_6) δ (ppm):172.9, 141.3, 130.2, 128.5, 126.2, 125.7, 111.7, 51.7; HRMS (ESI) *m/z*: [M-H]$^{-}$ calcd for $C_8H_4Cl_2NO$ 199.9670; found 199.9678.



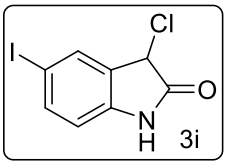
3,7-dichloroindolin-2-one (3g). Pale red solid; Yield (60 mg 70%) mp 178 °C; The title compound was prepared, according to the general procedure (A) as described above; FT-IR (KBr, cm^{-1}) 3161, 2934, 1732, 1719, 1623, 769, 744; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 11.23 (s, 1H), 7.37 (dd, J = 10.0, 8.0 Hz, 2H), 7.07 (t, J = 7.6 Hz, 1H), 5.68 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ (ppm): 173.5, 140.6, 130.6, 128.75, 124.8, 124.1, 114.7, 52.8; HRMS (ESI) *m/z*: [M+H]$^{+}$ calcd for $C_8H_6Cl_2NO$ 201.9826; found 201.9821.



5-bromo-3-chloroindolin-2-one (3h).[3] pale red solid; Yield (60 mg, 68%); mp 188-189 °C; The title compound was prepared, according to the general procedure (A) as described above; FT-IR (KBr, cm^{-1}) 325, 2926, 2853, 1744, 1616, 1444, 1381, 1297, 816, 657; ^{1}H NMR (400 MHz, $CDCl_3$+DMSO-d_6) δ (ppm):10.53 (s, 1H), 7.37 (s, 1H), 7.30 – 7.27 (m, 1H), 6.71 (d, J = 8.3 Hz, 1H), 5.05 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm):178.0, 146.4, 137.8, 133.4, 133.1, 119.4, 117.0, 56.4; HRMS (ESI) *m/z*: [M-H]$^{-}$ calcd for $C_8H_5BrClNO$ 243.9165; found 243.8507.

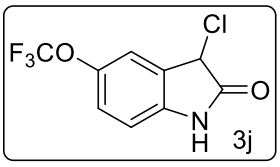


3-chloro-5-iodoindolin-2-one (3i). off white solid; Yield (61 mg, 70%); mp 180-181 °C; The



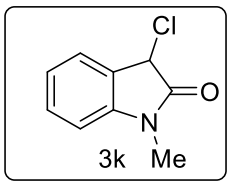
title compound was prepared, according to the general procedure (A) as described above; FT-IR (KBr, cm^{-1}) 3189, 2925, 1733, 1683, 1616, 1470, 1204, 820, 770; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm):10.88 (s, 1H), 7.67 – 7.63 (m, 2H), 6.73 (d, J = 8.0 Hz, 1H), 5.57 (s, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ (ppm):173.0, 142.6, 139.2, 134.3, 129.6, 113.0, 85.3, 51.9; HRMS (ESI) *m/z*: $[M-H]^-$ calcd for C_8H_4ClINO 291.9026; found 291.9041.

3-chloro-5-(trifluoromethoxy)indolin-2-one (3j). Off White solid; Yield (65 mg 73%); mp



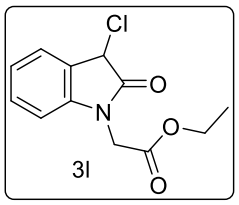
114.3- 116 °C; The title compound was prepared, according to the general procedure (A) as described above; FT-IR (KBr, cm^{-1}) 3259, 2924, 2853, 1745, 1628, 1487, 832, 611; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 10.95 (s, 1H), 7.42 (s, 1H), 7.33 (d, J = 8.2 Hz, 1H), 6.97 (d, J = 8.4 Hz, 1H), 5.63 (s, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ (ppm): 173.6, 143.8, 143.8, 142.1, 128.6, 124.2, 119.9, 111.6, 52.2; HRMS (ESI) m/z: $[M-H]^-$ calcd for $C_9H_4ClF_3NO_2$ 249.9883; found 249.9892.

3-chloro-1-methylindolin-2-one (3k). Off white solid; Yield (59 mg, 70%) mp 104 °C; The



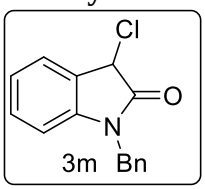
title compound was prepared, according to the general procedure (A) as described above; FT-IR (KBr, cm^{-1}) 3134, 2937, 1726, 1607, 1485, 818, 781, 640; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm):7.44 – 7.39 (m, 2H), 7.12 (t, J = 7.2 Hz, 1H), 7.07 (d, J = 7.6 Hz, 1H), 5.67 (s, 1H), 3.35 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ (ppm): 171.9, 144.2, 130.8, 126.14, 125.7, 123.4, 109.7, 52.1, 26.8; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_9H_8ClNNaO$ 204.0192; found 204.0191.

ethyl 2-(3-chloro-2-oxoindolin-1-yl)acetate (3l). Pale red solid; Yield (65 mg 76%); mp 109-

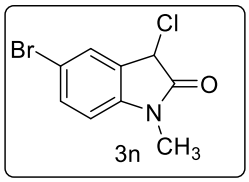


111; The title compound was prepared, according to the general procedure (A) as described above; FT-IR (KBr, cm^{-1}) 2983, 1741, 1725, 1613, 1236, 907, 753; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm):7.46 (d, J = 7.6 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.14 (td, J = 7.6, 0.8 Hz, 1H), 7.08 (d, J = 7.6 Hz, 1H), 5.82 (s, 1H), 4.60 (s, 2H), 4.16 (q, J = 7.2 Hz, 2H), 1.21 (t, J = 7.2 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ (ppm): 172.3, 168.0, 143.2, 130.8, 126.0, 125.9, 123.7, 110.0, 61.7, 51.7, 41.8, 14.5; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{12}H_{13}ClNO_3$ 254.0584; found 254.0575.

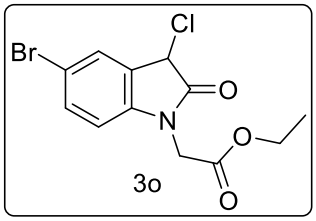
1-benzyl-3-chloroindolin-2-one (3m). White solid; Yield (65 mg 73%); mp 141- 144 °C; The title compound was prepared, according to the general procedure (A) as described above; FT-IR (KBr, cm^{-1}) 3231, 2926, 2852, 1719, 1611, 1344; ^1H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.44 (d, J = 7.6 Hz, 1H), 7.37 – 7.33 (m, 4H), 7.31 (s, 1H), 7.30 – 7.27 (m, 1H), 7.10 (t, J = 7.6 Hz, 1H), 6.97 (d, J = 7.6 Hz, 1H), 5.80 (s, 1H), 4.92 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ (ppm): 172.3, 143.2, 136.3, 130.8, 129.2, 128.1, 127.7, 126.2, 126.0, 123.6, 110.3, 52.1, 43.4; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{15}H_{13}ClNO$ 258.0686; found 258.0681.



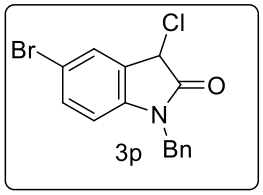
5-bromo-3-chloro-1-methylindolin-2-one (3n). Pale red solid; Yield (66 mg 74%); mp 158-160 °C; The title compound was prepared, according to the general procedure (A) as described above; FT-IR (KBr, cm^{-1}) 2937, 1722, 1608, 1488, 1345, 1102, 817, 775; ^1H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.61 (ddd, J = 4.4, 2.4, 0.8 Hz, 2H), 7.06 (d, J = 8.8 Hz, 1H), 5.68 (s, 1H), 3.15 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ (ppm):171.5, 143.6, 133.5, 128.5, 128.5, 114.9, 111.8, 51.5, 27.0; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_9H_8BrClNO$ 259.9478; found 259.9466.



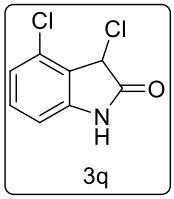
ethyl 2-(5-bromo-3-chloro-2-oxoindolin-1-yl)acetate (3o). Pale red solid; Yield (71 mg,78%) mp 109.3-110 °C; The title compound was prepared, according to the general procedure (A) as described above; FT-IR (KBr, cm^{-1}) 3567, 2982, 1735, 1613, 1488, 1376, 1229, 816; ^1H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.64 (s, 1H), 7.60 (dd, J = 8.4, 1.9 Hz, 1H), 7.09 (d, J = 8.4 Hz, 1H), 5.84 (s, 1H), 4.61 (s, 2H), 4.16 (q, J = 7.2 Hz, 2H), 1.21 (t, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ (ppm):171.8, 167.8, 142.6, 133.5, 128.8, 128.2, 115.3, 112.2, 61.8, 51.1, 42.0, 14.4; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{12}H_{12}BrClNO_3$ 331.9689; found 331.9686.



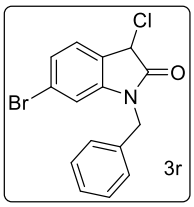
1-benzyl-5-bromo-3-chloroindolin-2-one (3p). pale red solid; Yield (66 mg, 74%); mp 127-129 °C; The title compound was prepared, according to the general procedure (A) as described above; FT-IR (KBr, cm^{-1}) 3420, 2926, 1708, 1608, 1480, 1333, 813, 743; ^1H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.65 (d, J = 1.2 Hz, 1H), 7.53 (dd, J = 8.4, 2.0 Hz, 1H), 7.36 – 7.29 (m, 5H), 6.95 (d, J = 8.4 Hz, 1H), 5.82 (s, 1H), 4.93 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ (ppm):171.9, 142.5, 136.0, 133.4, 129.2, 128.8, 128.6, 128.1, 127.6, 115.2, 112.3, 51.5, 43.5; HRMS (ESI) *m/z*: $[M-H]^-$ calcd for $C_{15}H_{10}BrClNO$ 333.9635; found 333.9643.



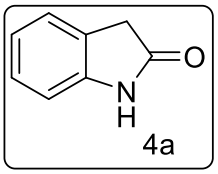
3,4-dichloroindolin-2-one(3q).[3] Pale red solid; Yield (67 mg, 79%); mp 168-169 °C; The title compound was prepared, according to the general procedure (A) as described above; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 10.99 (s, 1H), 7.37 – 7.32 (m, 1H), 7.08 (dd, J = 8.0, 0.8 Hz, 1H), 6.88 – 6.86 (m, 1H), 5.59 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ (ppm): 172.7, 144.8, 132.7, 131.4, 124.1, 122.9, 109.6, 51.9.



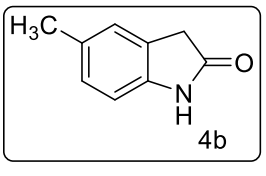
1-benzyl-6-bromo-3-chloroindolin-2-one (3r). Pale red solid; Yield (75 mg, 84%); mp 127-128 °C; The title compound was prepared, according to the general procedure (A) as described above; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.41 (dd, J = 8.0, 1.2 Hz, 1H), 7.37 (t, J = 1.2 Hz, 1H), 7.35 (dd, J = 3.6, 1.6Hz, 3H), 7.31 (d, J = 1.6 Hz, 1H), 7.29 (d, J = 1.6 Hz, 1H), 7.26 (d, J = 1.6 Hz, 1H), 5.79 (s, 1H), 4.95 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ (ppm): 172.2, 144.8, 136.0, 129.2, 128.1, 127.8, 127.7, 126.2, 125.6, 123.6, 113.2, 51.4, 43.4.



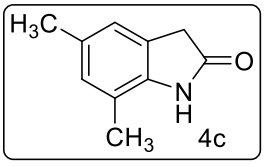
Indolin-2-one (4a). white solid; Yield (69 mg, 94%); mp 106-112 °C; The title compound was prepared, according to the general procedure (B) as described above; FT-IR (KBr, cm^{-1}) 3196, 3086, 3025, 2924, 1710, 1473, 1334, 1235, 744, 675; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 10.35 (s, 1H), 7.17 (dd, J = 18.4, 7.6 Hz, 2H), 6.91 (t, J = 7.6 Hz, 1H), 6.79 (s, 1H), 3.45 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ (ppm): 176.8, 144.1, 127.9, 126.2, 124.8, 121.6, 109.6, 36.2; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for C_8H_8NO 134.0606; found 134.0600.



5-methylindolin-2-one (4b). Off white solid; Yield (55 mg, 80%); mp 147-150 °C; The title compound was prepared, according to the general procedure (B) as described above; FT-IR (KBr, cm^{-1}) 3153, 2918, 2854, 1695, 1488, 1247, 1214, 819, 669; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 10.24 (s, 1H), 7.01 (s, 1H), 6.95 (d, J = 8.4 Hz, 1H), 6.68 (d, J = 7.6 Hz, 1H), 3.40 (s, 2H), 2.23 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ (ppm): 176.8, 141.6, 130.4, 128.1, 126.3, 125.6, 109.3, 36.2, 21.1; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_9H_{10}NO$ 148.0757; found 148.0758.

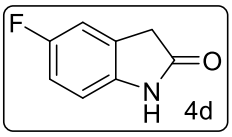


5,7-dimethylindolin-2-one (4c). White solid; Yield (50 mg, 71%); mp 196-199 °C; The title compound was prepared, according to the general procedure (B) as described above; FT-IR (KBr, cm^{-1}) 3154, 2934, 2853, 1704, 1624, 1474, 1223, 850, 722; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 10.30 (s, 1H), 6.81 (d, J = 19.6 Hz, 2H), 3.41 (s, 2H), 2.20 (s, 3H), 2.15 (s, 3H); ^{13}C{^{1}H} NMR (100



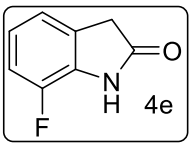
MHz, DMSO-d_6) δ (ppm): 177.2, 140.3, 130.3, 129.5, 125.9, 122.8, 118.5, 36.5, 21.0, 16.9; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{10}H_{12}NO$ 162.0913; found 162.0910.

5-fluoroindolin-2-one (4d). Off white solid; Yield (50 mg, 73%); mp 122-125 °C; The title



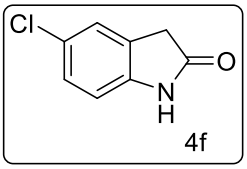
compound was prepared, according to the general procedure (B) as described above; FT-IR (KBr, cm^{-1}) 3181, 3050, 2927, 1696, 1484, 812, 672; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 10.36 (d, J = 0.4 Hz, 1H), 7.13 – 7.08 (m, 1H), 6.99 (td, J = 9.6, 2.4 Hz, 1H), 6.78 (dd, J = 8.4, 4.4 Hz, 1H), 3.50 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ (ppm): 176.7, 159.4, (d, $^1J_{C\text{-}F}$ = 234.14 Hz), 140.4, (d, $^4J_{C\text{-}F}$ = 1,26 Hz), 128.2, (d, $^3J_{C\text{-}F}$ = 9 Hz), 114.1, (d, $^3J_{C\text{-}F}$ = 23.03 Hz), 112.8, (d, $^2J_{C\text{-}F}$ = 24.5 Hz), 110.1, (d, $^2J_{C\text{-}F}$ = 8.24 Hz), 36.7, 36.7; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for C_8H_7FNO 152.0512; found 152.0506.

7-fluoroindolin-2-one (4e). Pale red solid; Yield (50 mg, 73%); mp 184- 186 °C; The title



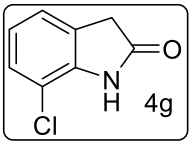
compound was prepared, according to the general procedure (B) as described above; FT-IR(KBr, cm^{-1}) 3181, 3050, 2927, 1696, 1484, 812, 672; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 10.84 (s, 1H), 7.07 (dd, J = 13.2, 8.2 Hz, 2H), 6.93 (td, J = 7.6, 4.8 Hz, 1H), 3.55 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ (ppm): 176.5, 147.8, (d, $^1J_{C\text{-}F}$ = 239.65 Hz), 131.1, (d, $^2J_{C\text{-}F}$ = 11.95 Hz),, 129.4, (d, $^3J_{C\text{-}F}$ = 4 Hz), 122.4, (d, $^3J_{C\text{-}F}$ = 5.84 Hz), 121.3, (d, $^4J_{C\text{-}F}$ = 2.6 Hz), 115.0, (d, $^2J_{C\text{-}F}$ = 17.04 Hz), 36.5, 36.4; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for C_8H_7FNO 152.0506; found 152.0503.

5-chloroindolin-2-one (4f). Off white solid; Yield (58 mg, 81%); mp 180- 183 °C; The title



compound was prepared, according to the general procedure (B) as described above; FT-IR (KBr, cm^{-1}) 3161, 3091, 2921, 2852, 1698, 1474, 1172, 817, 654; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 10.49 (s, 1H), 7.26 (d, J = 2.1 Hz, 1H), 7.21 (dd, J = 8.2, 2.2 Hz, 1H), 6.80 (d, J = 8.2 Hz, 1H), 3.50 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ (ppm): 176.5, 143.1, 128.5, 127.7, 125.6, 125.0, 111.0, 36.3.

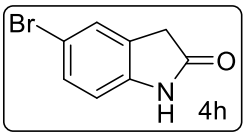
7-chloroindolin-2-one (4g). Pale red; Yield (55 mg, 78%); mp 186- 191 °C; The title



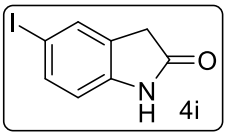
compound was prepared, according to the general procedure (B) as described above; FT-IR (KBr, cm^{-1}) 3192, 2940, 1699, 1621, 1324, 1136, 711; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 10.77 (s, 1H), 7.22 (dd, J = 8.0, 0.8 Hz, 1H), 7.18 – 7.15 (m, 1H), 6.94 (dd, J = 8.0, 7.2 Hz, 1H), 3.59 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz,

DMSO-d_6) δ (ppm): 176.6, 141.7, 128.2, 127.9, 123.5, 122.9, 113.8, 36.9; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for C_8H_7ClNO 168.0211; found 168.0207.

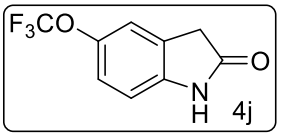
5-bromoindolin-2-one(4h). Off white solid; Yield (50 mg, 66%); mp 187-189 °C; The title compound was prepared, according to the general procedure (B) as described above; FT-IR (KBr, cm^{-1}) 3169, 1697, 1472, 1309, 816, 778; ^1H NMR (400 MHz, DMSO-d_6) δ (ppm):10.47 (s, 1H), 7.37 (s, 1H), 7.33 (dd, *J* = 8.0, 1.8 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 3.50 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ (ppm):176.4, 143.5, 130.5, 129.0, 127.7, 113.3, 111.4, 36.2; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for C_8H_7BrNO 211.9711; found 211.9703.



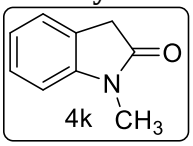
5-iodoindolin-2-one (4i). Off white solid; Yield (59 mg, 75%); mp 209-212 °C; The title compound was prepared, according to the general procedure (B) as described above; FT-IR (KBr, cm^{-1}) 3146, 3036, 2924, 2852, 1702, 1609, 1472, 1307, 1237, 817, 674; ^1H NMR (400 MHz, DMSO-d_6) δ (ppm): 10.46 (s, 1H), 7.50 (d, *J* = 9.2 Hz, 2H), 6.66 (d, *J* = 7.8 Hz, 1H), 358.48 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ (ppm):176.2, 143.9, 136.4, 133.2, 129.3, 111.9, 84.6, 36.0; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for C_8H_7INO 259.9572; found 259.9559.

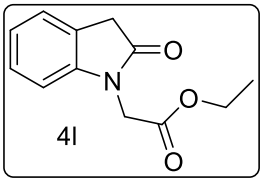


5-(trifluoromethoxy)indolin-2-one (4j). Off white solid; Yield (55 mg 72%); mp 140- 144 °C; The title compound was prepared, according to the general procedure (B) as described above; FT-IR (KBr, cm^{-1}) 3294, 2927, 1703, 1626, 1488, 834, 677; ^1H NMR (400 MHz, DMSO-d_6) δ (ppm): 10.52 (s, 1H), 7.24 (s, 1H), 7.16 (d, *J* = 8.6 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 3.54 (s, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ (ppm): 176.7, 143.4, 143.3, 143.2, 128.2, 122.0, 121.1, 119.6, 119.5, 118.7, 110.1, 36.5; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_9H_7F_3NO_2$ 218.0423; found 218.0423.

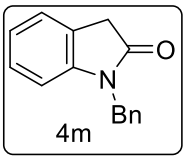


1-methylindolin-2-one (4k). white solid; Yield (50 mg, 64%); mp 165-169 °C; The title compound was prepared, according to the general procedure (B) as described above; FT-IR (KBr, cm^{-1}) 2923, 2852, 1701, 168, 1489, 1270, 1128, 662; ^1H NMR (400 MHz, DMSO-d_6) δ (ppm):7.30 – 7.25 (m, 2H), 7.01 (td, *J* = 7.6, 0.8 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 3.54 (s, 2H), 3.11 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ (ppm): 174.8, 145.5, 128.0, 125.2, 124.6, 122.3, 108.7, 35.6, 26.3; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_9H_{10}NO$ 148.0762; found 148.0750.

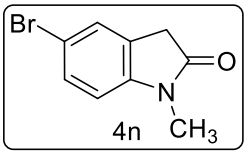


ethyl 2-(2-oxoindolin-1-yl)acetate (4l). White solid; Yield (60 mg, 68%); mp 125- 129 °C; 

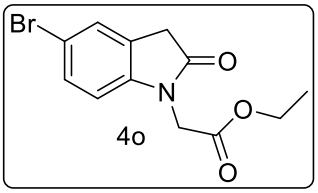
The title compound was prepared, according to the general procedure (B) as described above; FT-IR (KBr, cm^{-1}) 2985, 2925, 1740, 1715, 1352, 898, 756; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.29 (d, J = 7.2 Hz, 1H), 7.25 (t, J = 7.8 Hz, 1H), 7.03 (t, J = 7.4 Hz, 1H), 6.96 (d, J = 7.8 Hz, 1H), 4.54 (s, 2H), 4.15 (q, J = 7.2 Hz, 2H), 3.63 (s, 2H), 1.21 (t, J = 7.1 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ (ppm): 174.9, 168.4, 144.4 127.9, 124.9, 124.8, 122.5, 109.1, 61.5, 41.4, 35.3, 14.5; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{12}H_{14}NO_3$ 220.0968; found 220.0971.

1-benzylindolin-2-one (4m). off white solid; Yield (50 mg, 77%); mp 140- 142 °C; The title 

compound was prepared, according to the general procedure (B) as described above; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.33 (d, J = 4.4 Hz, 4H), 7.29 – 7.25 (m, 2H), 7.18 (td, J = 7.6, 1.2 Hz, 1H), 6.99 (td, J = 7.6, 1.2 Hz, 1H), 6.87 (d, J = 7.6 Hz, 1H), 4.89 (s, 2H), 3.67 (s, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ (ppm):175.0, 144.5, 137.0, 129.0, 127.9, 127.8, 127.7, 125.3, 124.8, 122.4, 109.3, 43.0, 35.6; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{15}H_{14}NO$ 224.1075; found 224.1073.

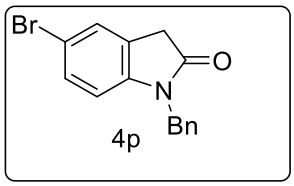
5-bromo-1-methylindolin-2-one (4n). White solid; Yield (60 mg, 78%); mp 128- 132 °C; The 

title compound was prepared, according to the general procedure (B) as described above; FT-IR (KBr, cm^{-1}) 2942, 1714, 1609, 1489, 1334; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.47 – 7.43 (m, 2H), 6.94 (d, J = 8.0 Hz, 1H), 3.57 (s, 2H), 3.10 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ (ppm): 174.3, 144.8, 130.6, 128.0, 127.4, 114.0, 110.6, 35.6, 26.4; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for C_9H_8BrNO 225.9862; found 225.9864.

ethyl 2-(5-bromo-2-oxo-2,3-dihydro-1H-inden-1-yl)acetate (4o). off white solid; Yield (63 

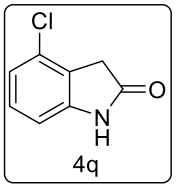
mg, 78%); mp 107 °C; The title compound was prepared, according to the general procedure (B) as described above; FT-IR (KBr, cm^{-1}) 2978, 2926, 1718, 1729, 1488, 1230, 810, 673; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.48 (s, 1H), 7.44 (dd, J = 8.0, 2.0 Hz, 1H), 6.96 (d, J = 8.0 Hz, 1H), 4.54 (s, 2H), 4.15 (d, J = 7.2 Hz, 2H), 3.69 (s, 2H), 1.21 (t, J = 7.2 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ (ppm): 174.6, 168.3, 143.8, 130.6, 127.7, 127.6, 114.3, 111.0, 61.6, 4.5, 35.3, 14.5; HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $C_{12}H_{12}BrNNaO_3$ 319.9893; found 319.9918.

1-benzyl-5-bromoindolin-2-one (4p). off white solid; Yield (54 mg, 67%); mp 118- 121 °C;



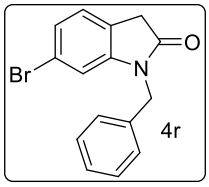
The title compound was prepared, according to the general procedure (B) as described above; FT-IR (KBr, cm^{-1}) 2926, 1703, 1606, 1483, 1339, 1274, 729, 699; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.46 (dt, J = 2.4, 1.2 Hz, 1H), 7.37 (dd, J = 8.4, 2.0 Hz, 1H), 7.33 – 7.27 (m, 5H), 6.82 (d, J = 8.4 Hz, 1H), 4.89 (s, 2H), 3.72 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ (ppm): 143.8, 136.7, 130.5, 129.1, 128.0, 127.9, 127.7, 127.7, 114.2, 111.1, 43.0, 35.6; HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{15}H_{13}BrNO$ 302.0175; found 302.0179.

4-chloroindolin-2-one (4q). white solid; Yield (60 mg, 87%); mp 185-187 °C; The title



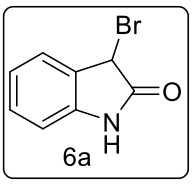
compound was prepared, according to the general procedure (B) as described above; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 10.59 (s, 1H), 7.23 – 7.19 (m, 1H), 6.98 (dd, J = 8.4, 0.8 Hz, 1H), 6.79 (d, J = 7.6 Hz, 1H), 3.50 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ (ppm): 175.6, 145.5, 129.8, 129.4, 124.6, 121.4, 108.4, 35.7.

1-benzyl-6-bromoindolin-2-one(4r). white solid; Yield (62 mg, 77%); mp 121- 122 °C; The



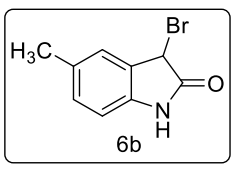
title compound was prepared, according to the general procedure (B) as described above; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.37 – 7.34 (m, 1H), 7.33 (d, J = 2.0 Hz, 3H), 7.29 (s, 1H), 7.25 – 7.22 (m, 1H), 7.17 (dd, J = 7.6, 1.6 Hz, 1H), 7.10 (d, J = 1.6 Hz, 1H), 4.91 (s, 2H), 3.66 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ (ppm): 172.3, 144.8, 136.0, 129.2, 128.1, 127.8, 127.6, 126.3, 125.6, 123.6, 113.3, 51.5, 43.4.

3-bromoindolin-2-one (6a).[3] off white solid; yield (53 mg, 73%); mp 71-72 °C; The title



compound was prepared, according to the general procedure (C) as described above; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm):10.77 (s, 1H), 7.34 (d, J = 7.6 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.04 – 7.00 (m, 1H), 6.86 (d, J = 7.6 Hz, 1H), 5.71 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ (ppm): 174.0, 142.9, 130.7, 127.5, 126.4, 122.8, 110.7.

3-bromo-5-methylindolin-2-one (6b).[3] off white solid; Yield (60 mg, 81%); mp 168-169 °C;



The title compound was prepared, according to the general procedure (C) as described above; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.03 (s, 1H), 7.13 (s, 1H), 7.02 – 6.99 (m, 1H), 6.75 (d, J = 8.0 Hz, 1H), 5.19 (s, 1H), 2.26 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)) δ (ppm): 175.3, 138.7, 133.1, 131.0, 126.8, 126.7, 110.5, 39.4, 21.0

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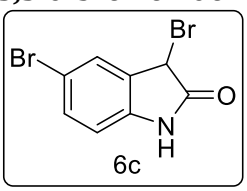
3,5-dibromoindolin-2-one (6c).[3] off white solid; Yield (55 mg, 70%); mp 139-140 °C; The title compound was prepared, according to the general procedure (C) as described above; ^{1}H NMR (400 MHz, $CDCl_3$+DMSO-d_6) δ (ppm) 10.37 (s, 1H), 7.36 (d, J = 2.0 Hz, 1H), 7.26 (dd, J = 8.4, 2.0 Hz, 1H), 6.69 (d, J = 8.0 Hz, 1H), 5.13 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$+DMSO-d_6) δ (ppm): 173.7, 141.4, 133.0, 129.0, 128.8, 114.8, 112.1, 38.9.

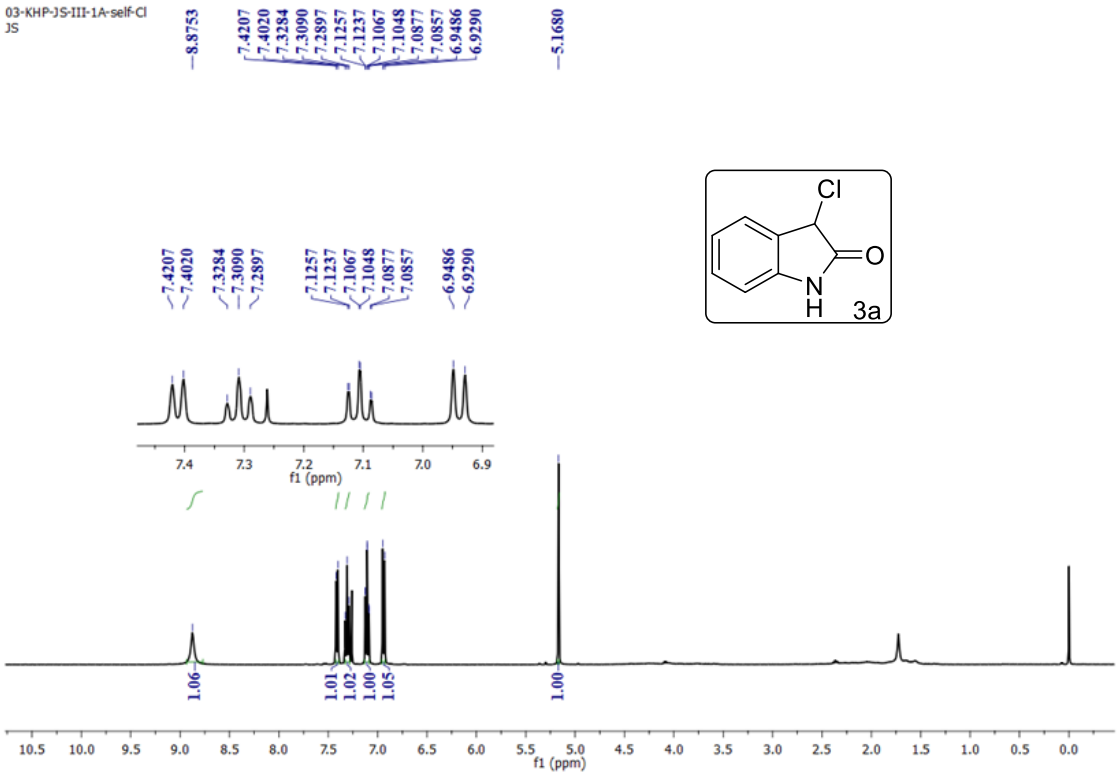


6c

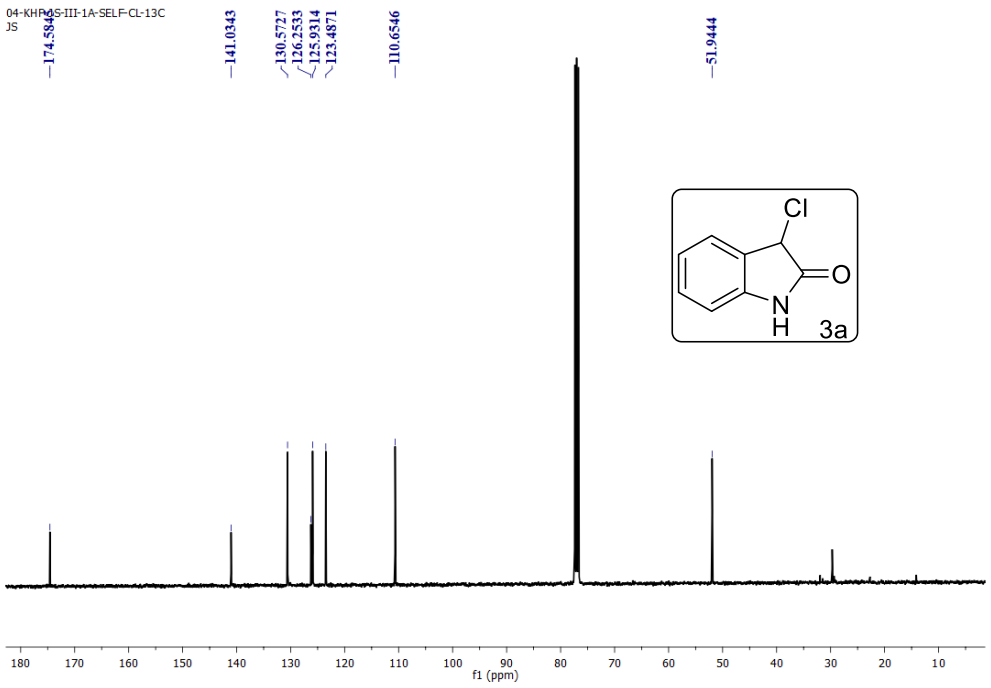
References

1. A. N. C. Lötter, R. Pathak, T. S. Sello, M. A. Fernandes, W. A. L. van Otterlo and C. B. de Koning, *Tetrahedron*, 2007, **63**, 2263–2274.
2. S. Rossiter, *Tetrahedron Lett.*, 2002, **43**, 4671-4673.
3. L. Liu, Y. Li, T. Huang, D. Kong and M. Wu, *Beilstein J. Org. Chem.*, 2021, **17**, 2321-2328.

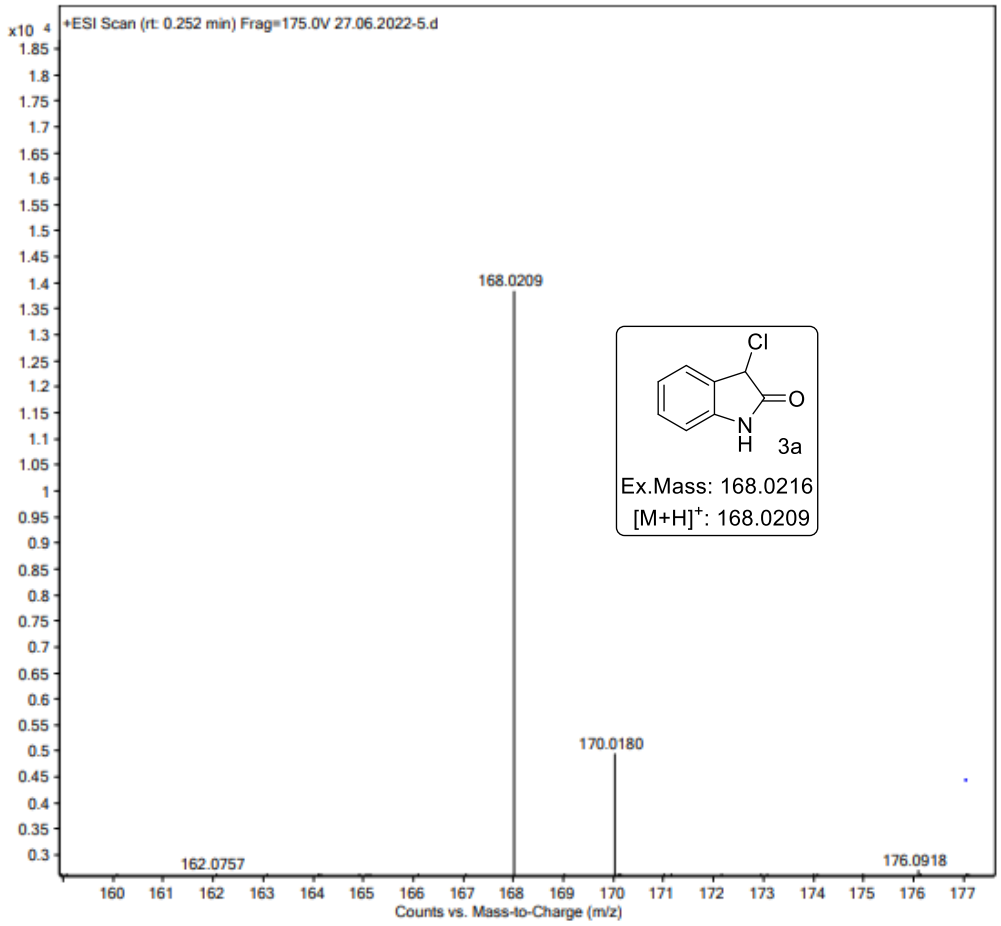
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 3-chloroindolin-2-one (3a)



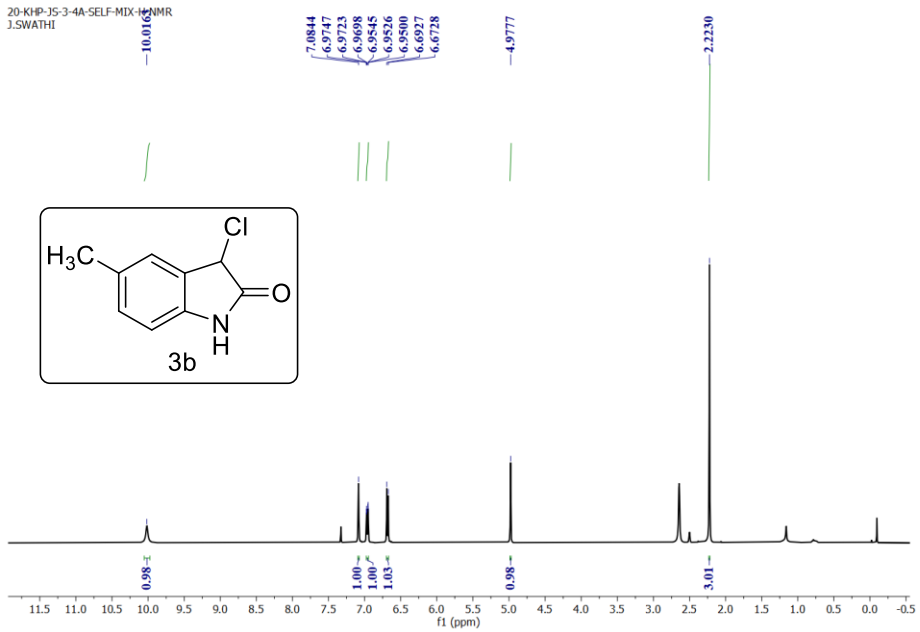
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of 3-chloroindolin-2-one (3a)



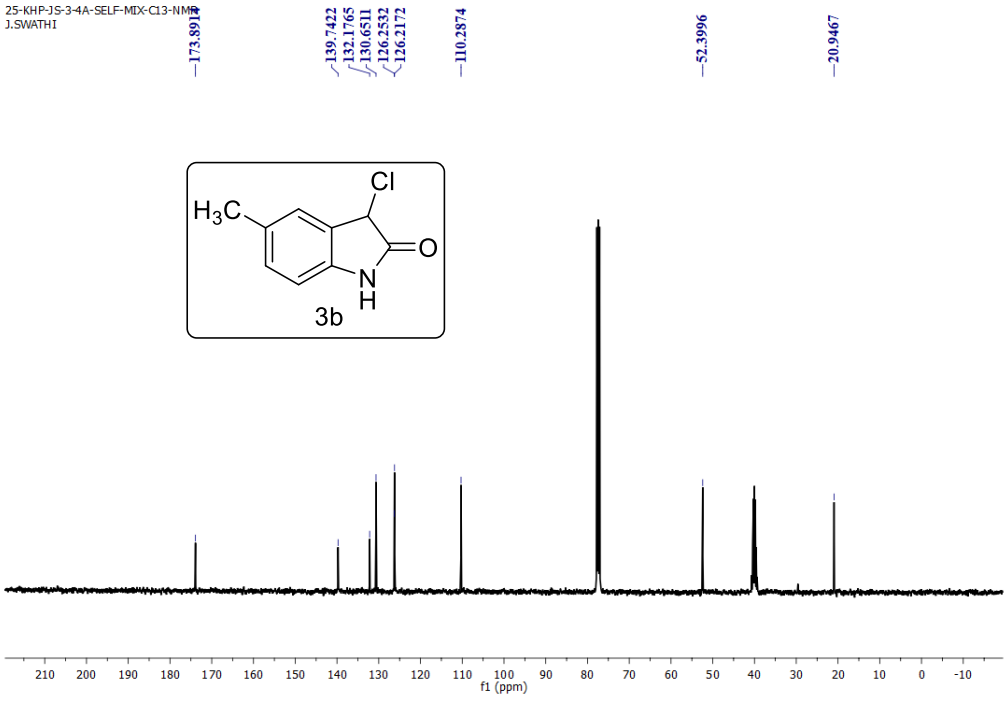
HRMS of 3-chloroindolin-2-one (3a)



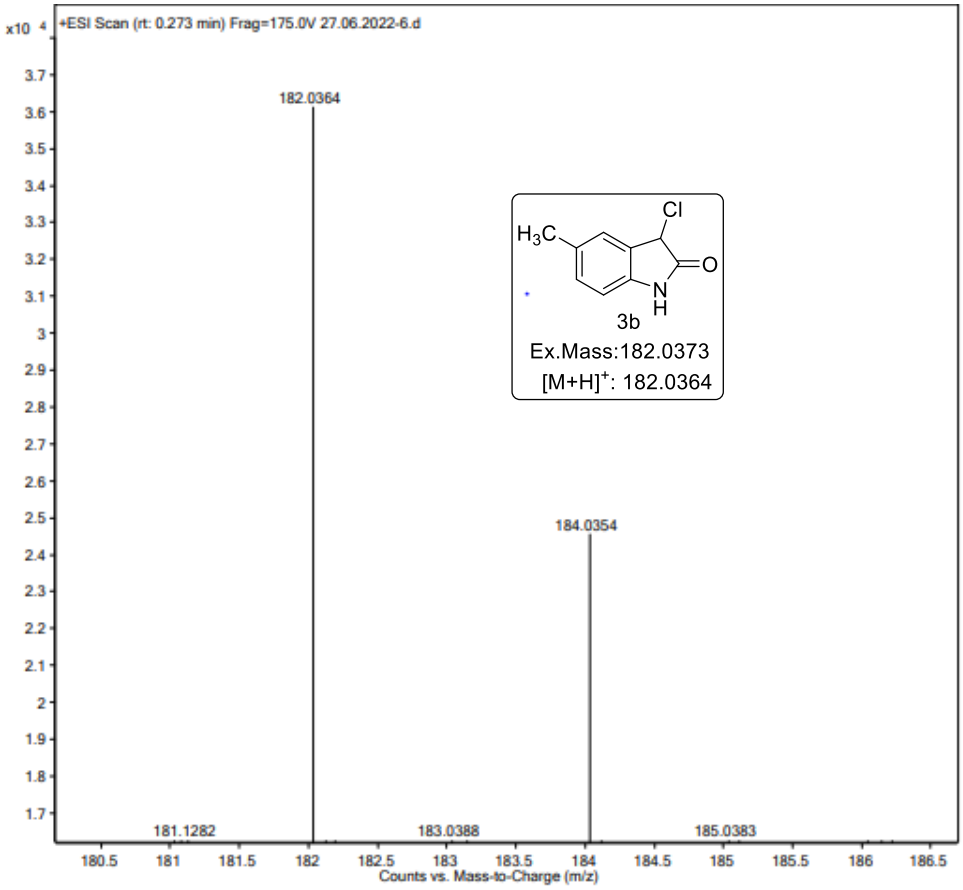
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 3-chloro-5-methylindolin-2-one (3b)



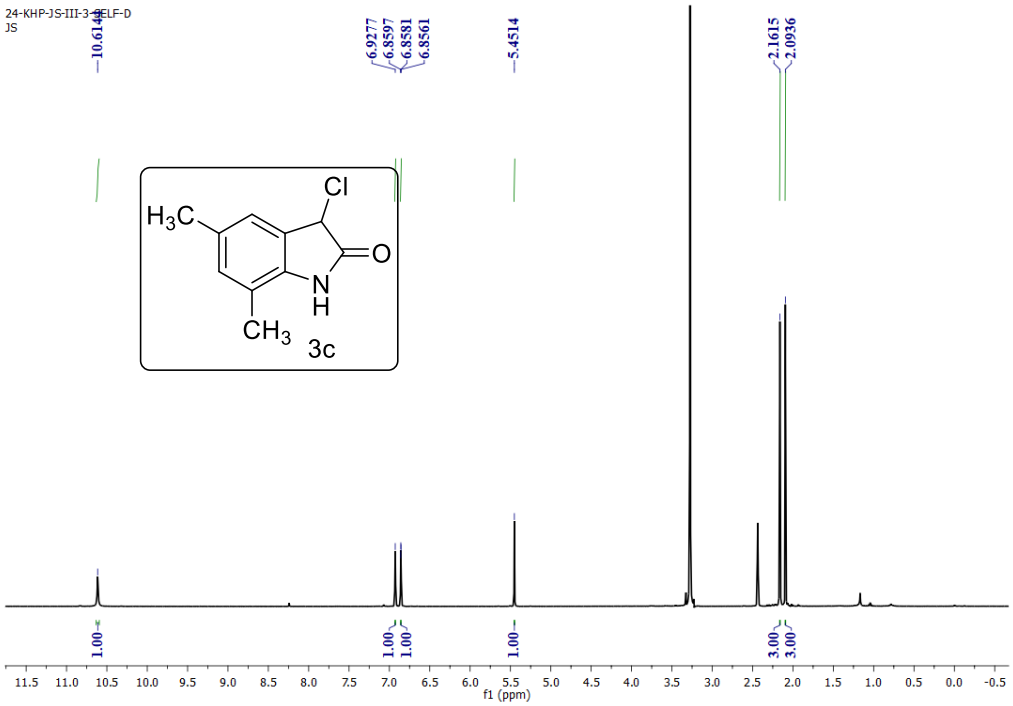
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6 + $CDCl_3$) spectrum of 3-chloro-5-methylindolin-2-one (3b)



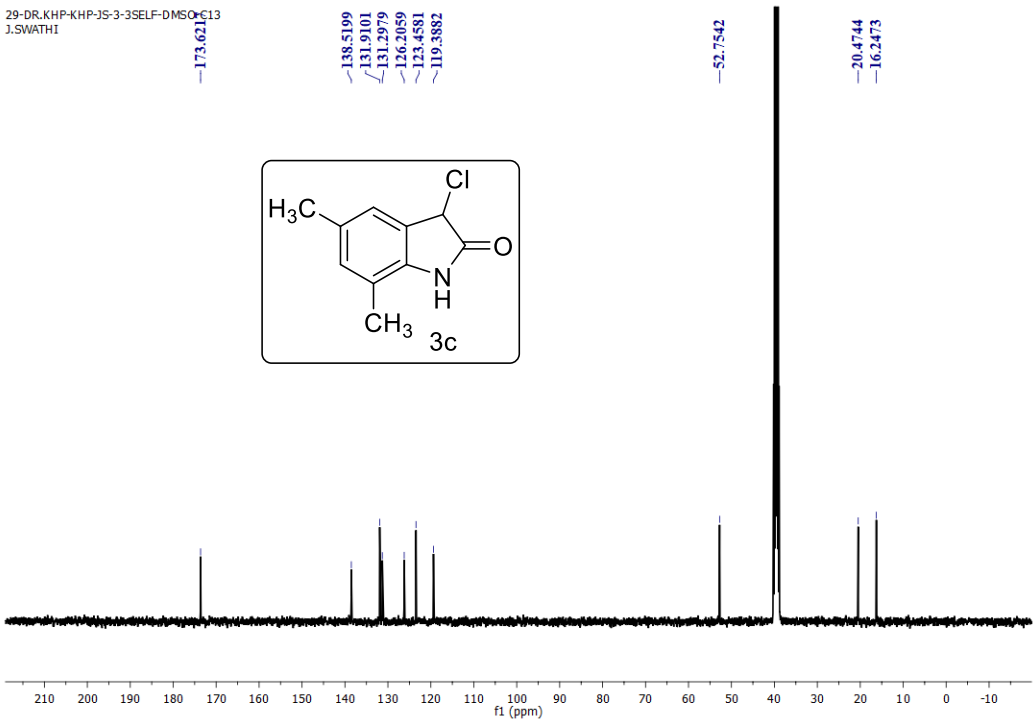
HRMS of 3-chloro-5-methylindolin-2-one (3b)



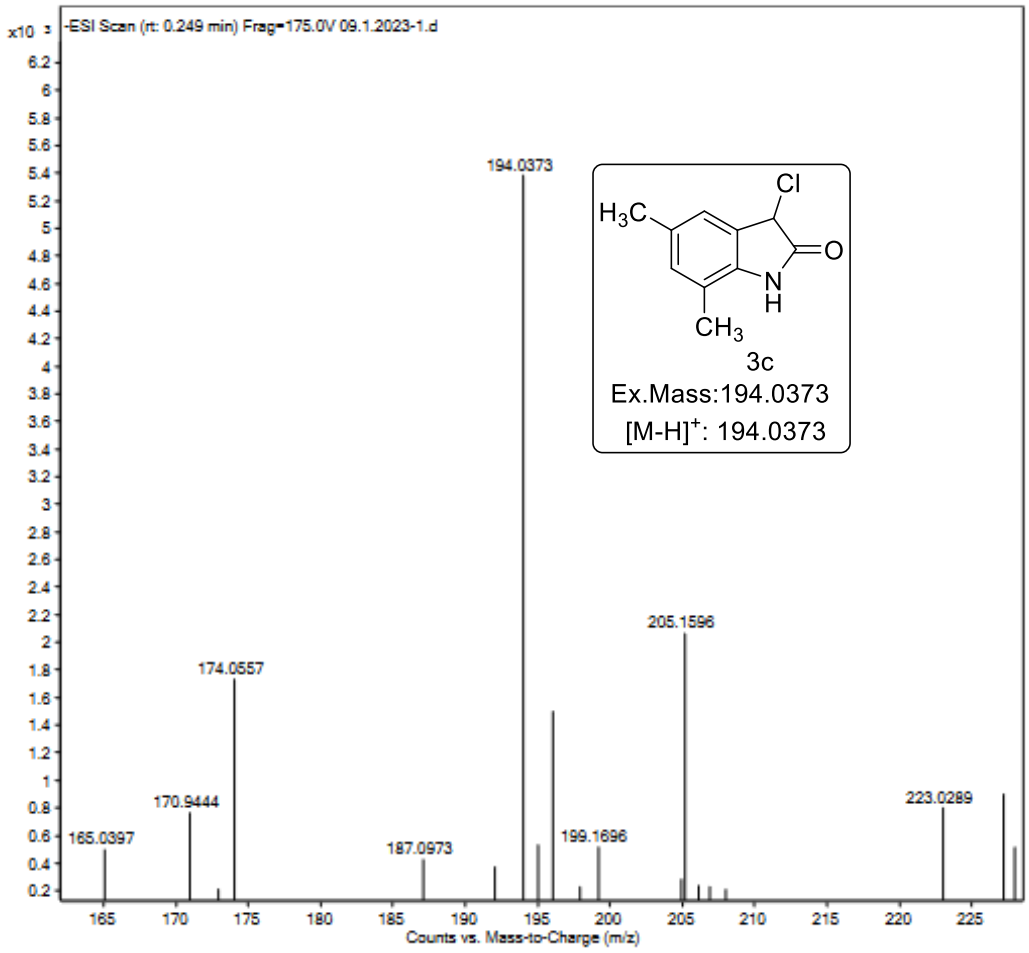
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 3-chloro-5,7-dimethylindolin-2-one (3c).



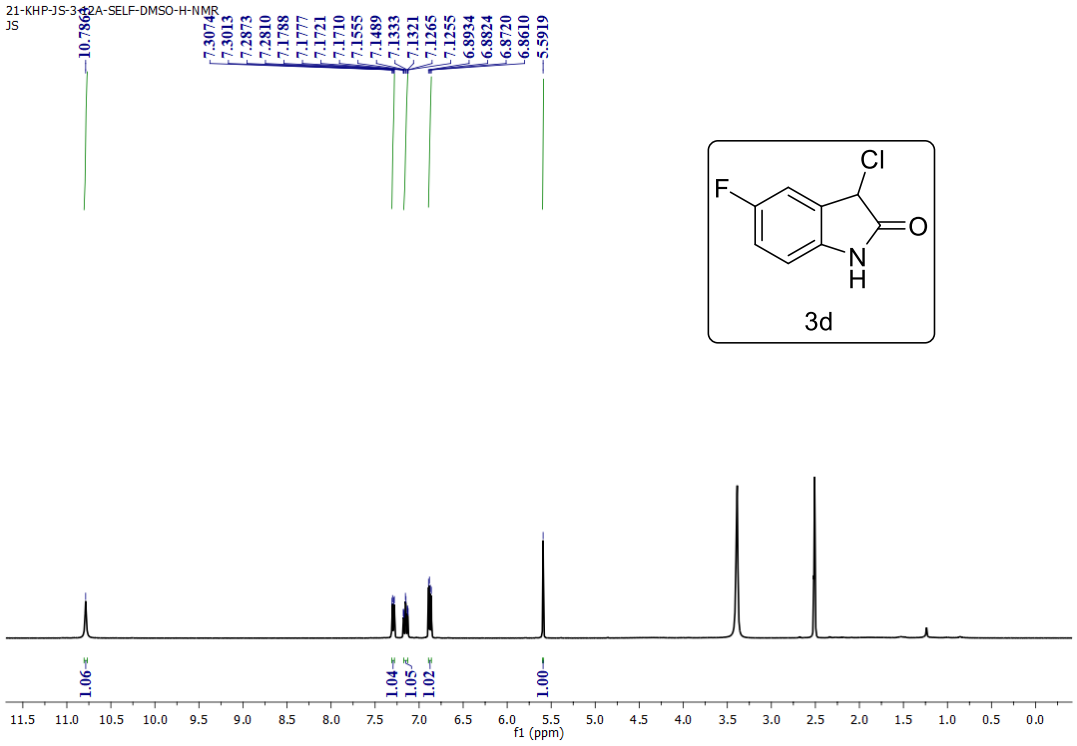
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of 3-chloro-5,7-dimethylindolin-2-one (3c).



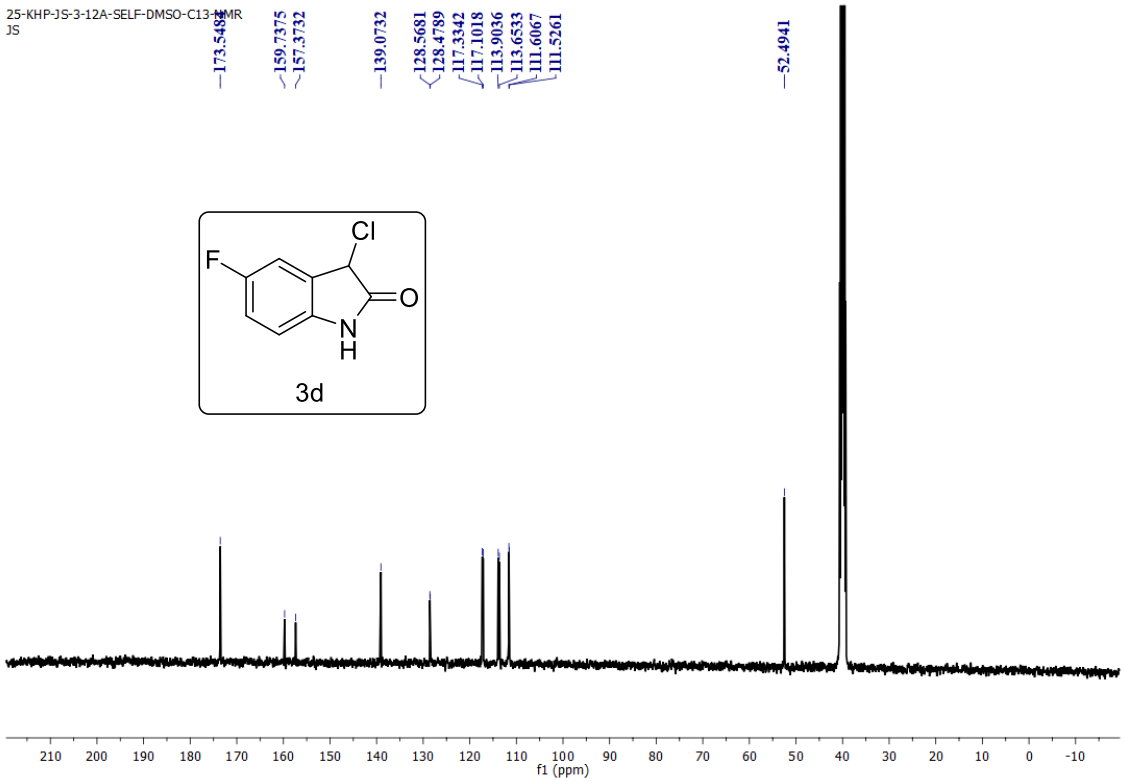
HRMS of 3-chloro-5,7-dimethylindolin-2-one (3c)



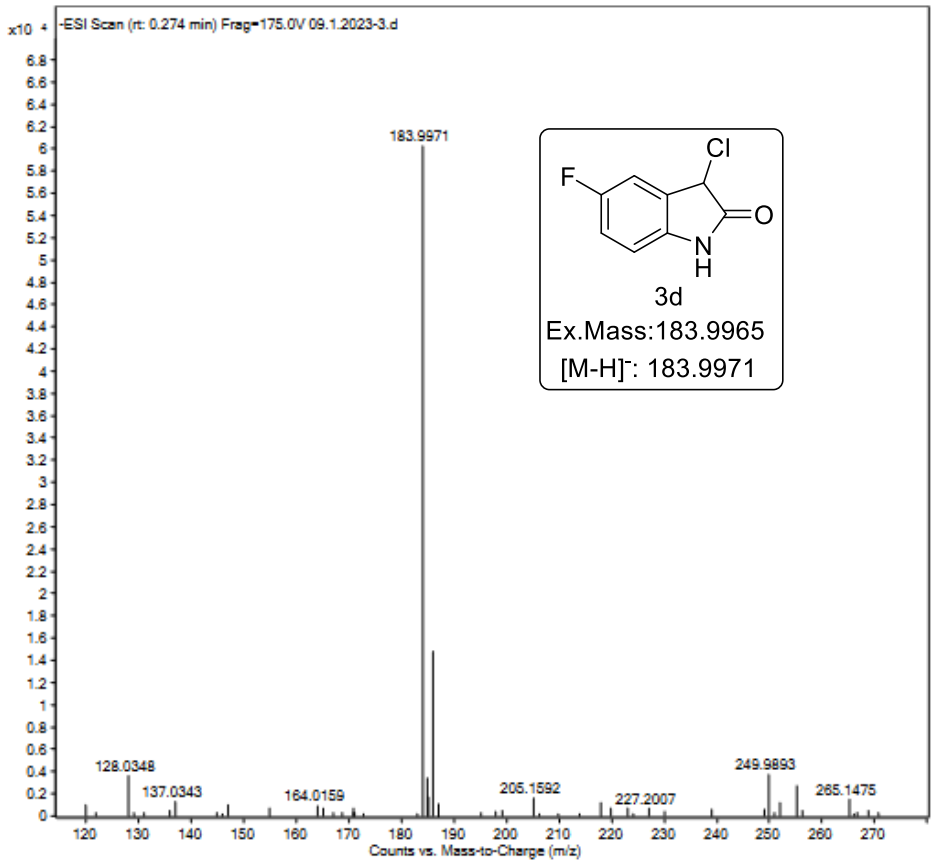
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 3-chloro-5-fluoroindolin-2-one (3d)



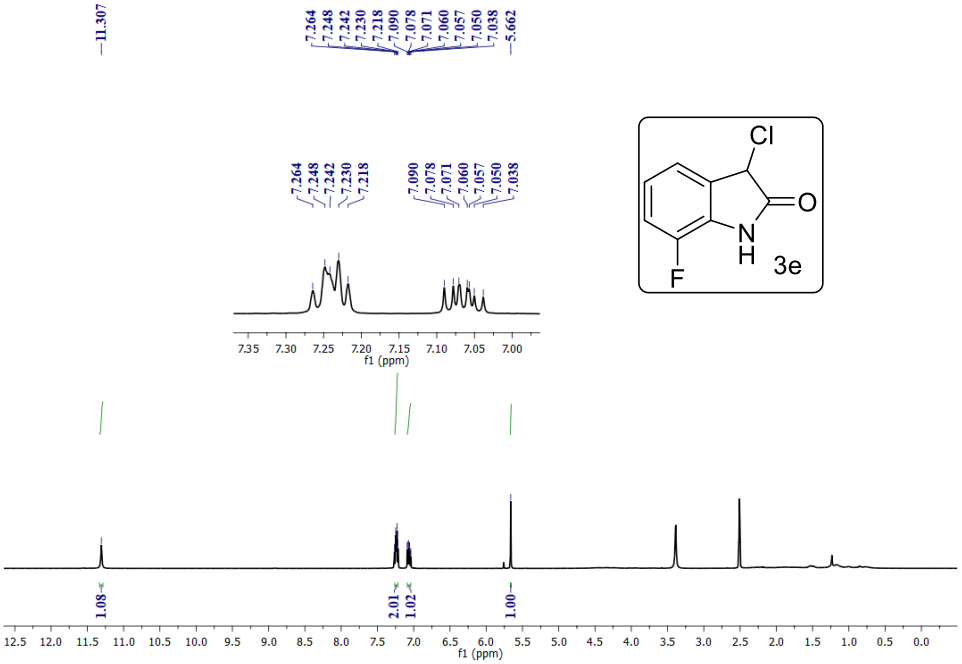
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of 3-chloro-5-fluoroindolin-2-one (3e)



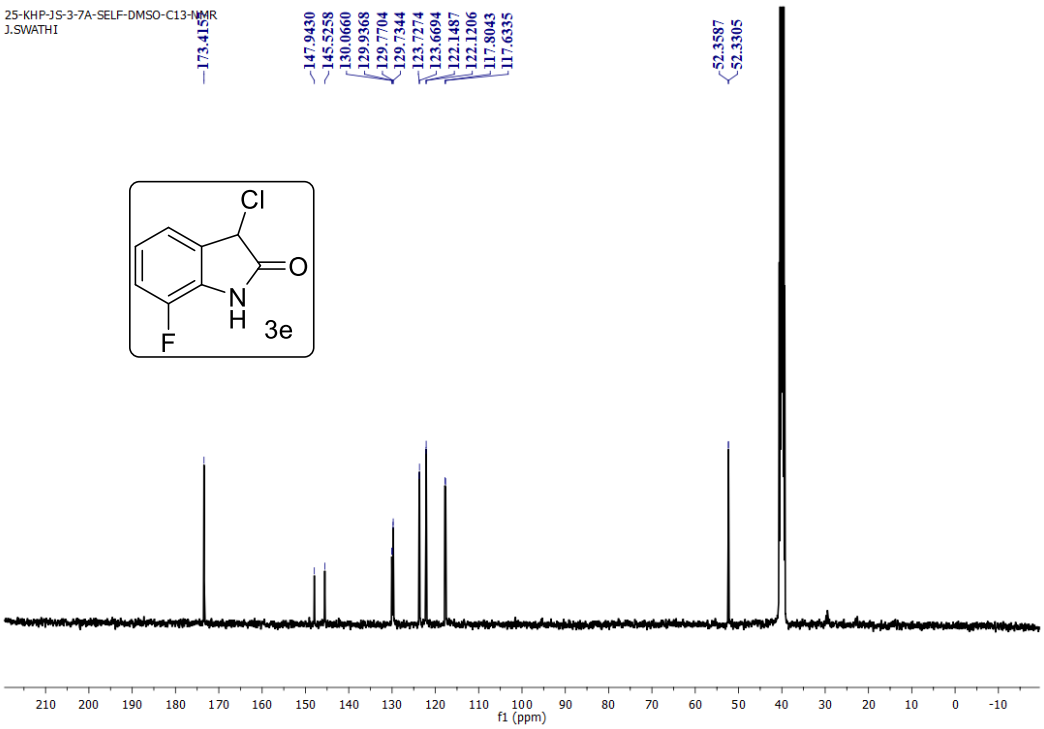
HRMS of 3-chloro-5-fluoroindolin-2-one (3d)



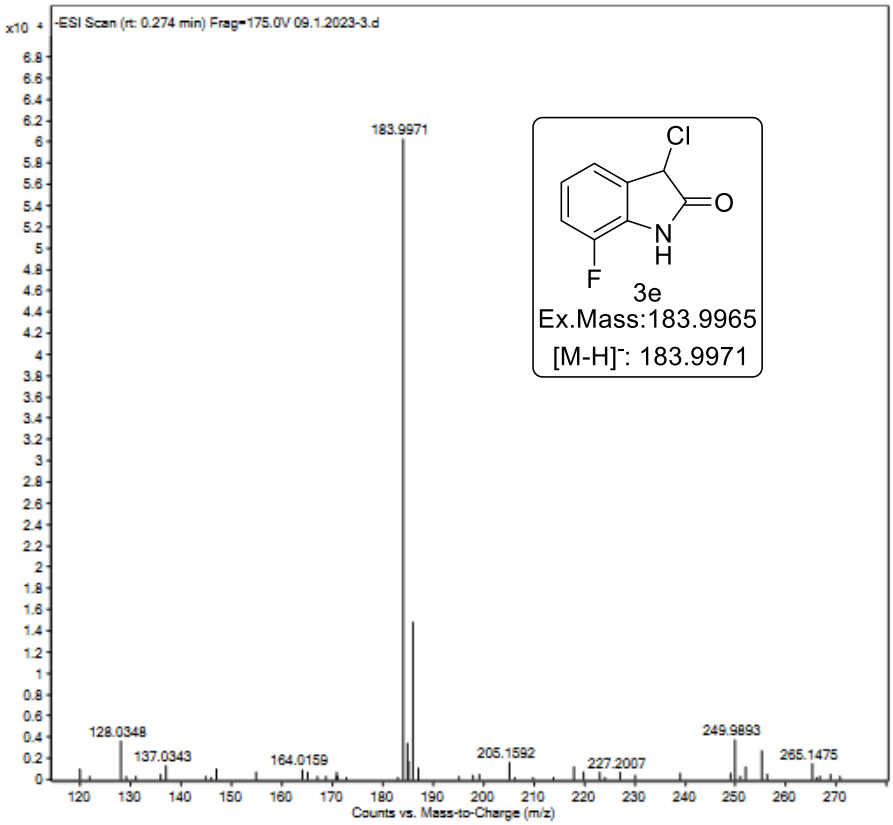
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 3-chloro-7-fluoroindolin-2-one (3e)



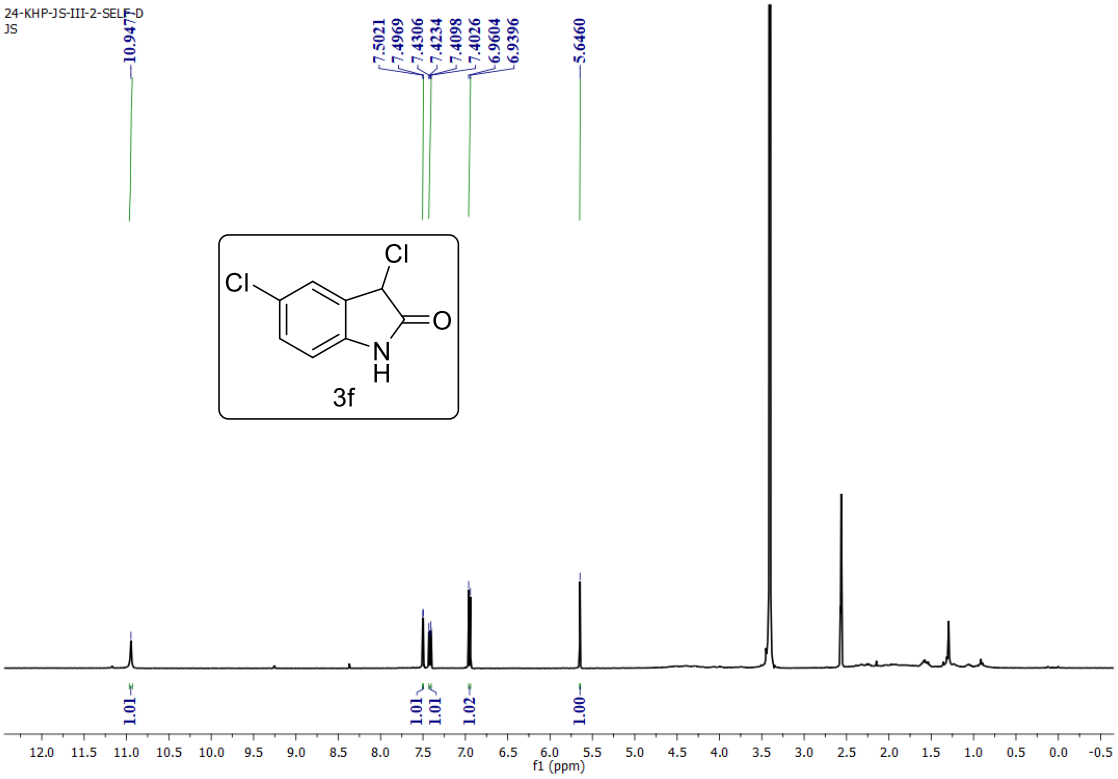
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of 3-chloro-7-fluoroindolin-2-one (3e)



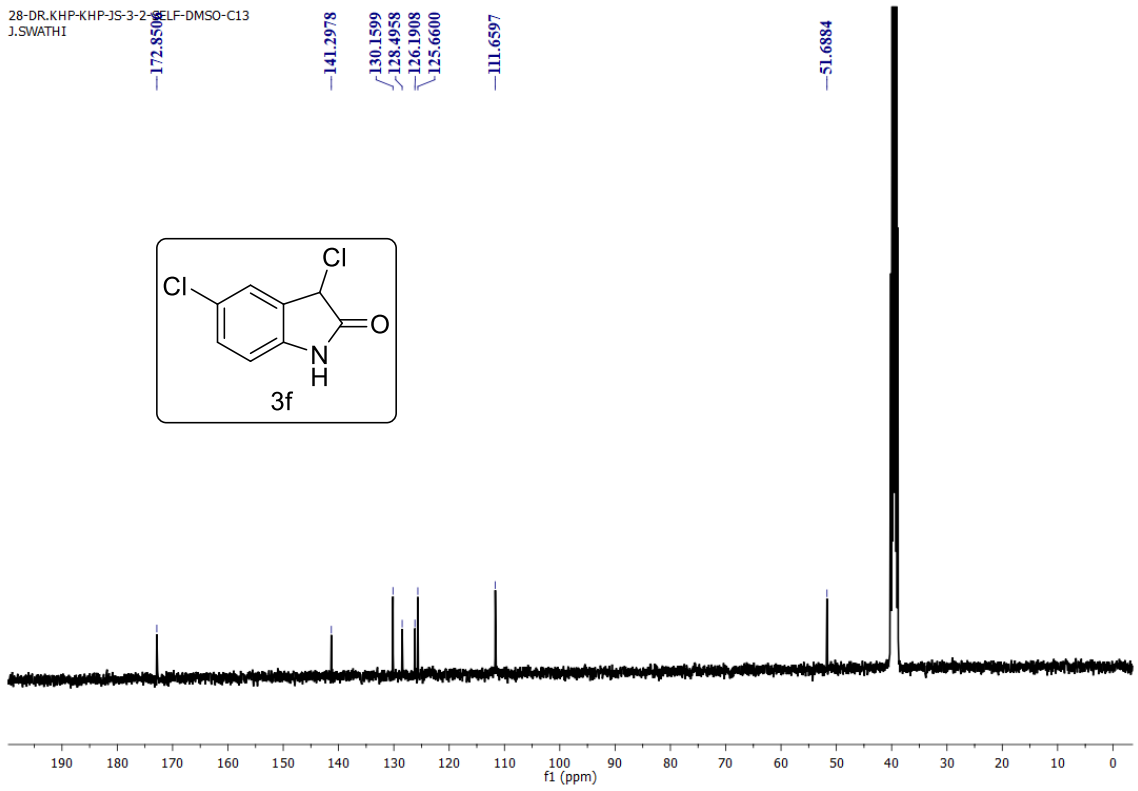
HRMS of 3-chloro-7-fluoroindolin-2-one (3e)



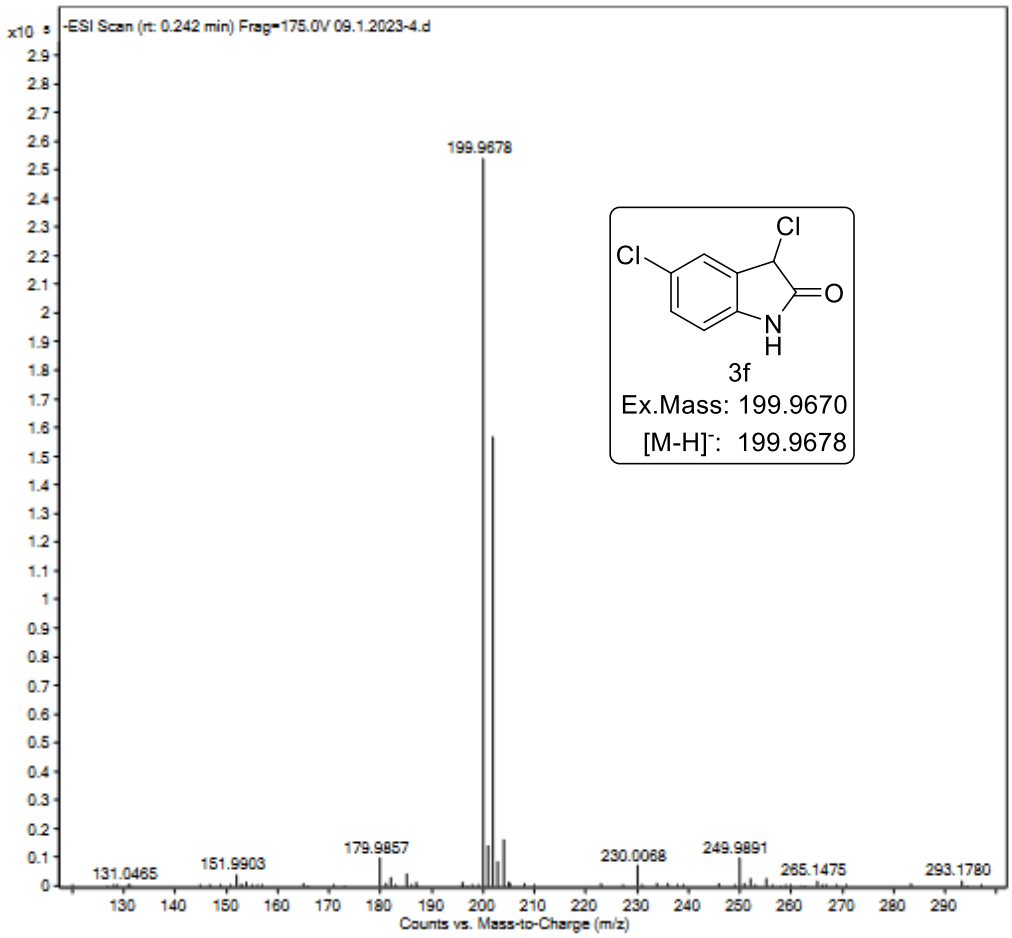
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 3,5-dichloroindolin-2-one (3f)



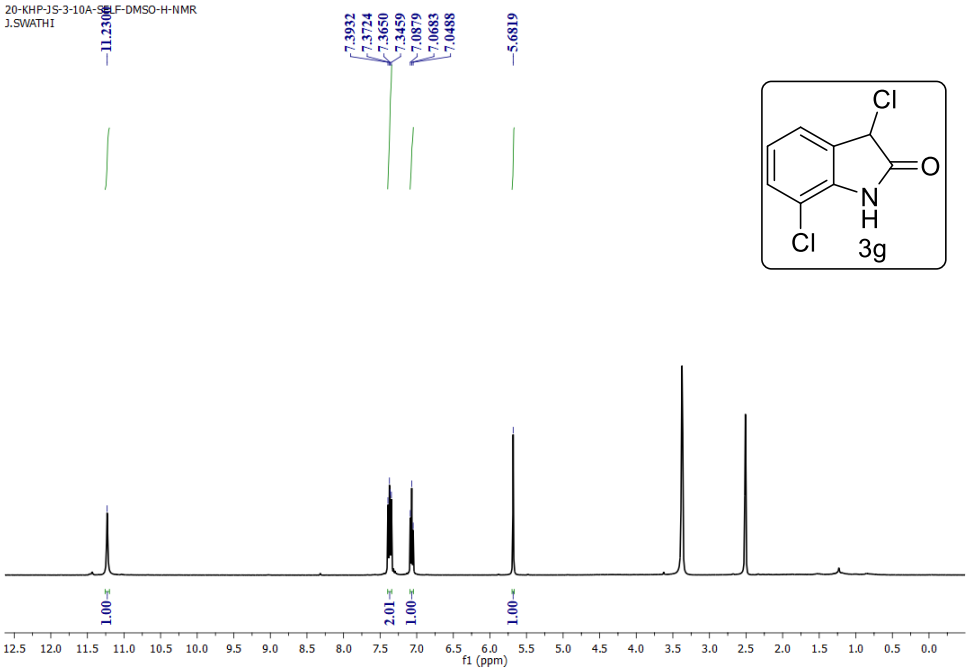
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of 3,5-dichloroindolin-2-one (3f)



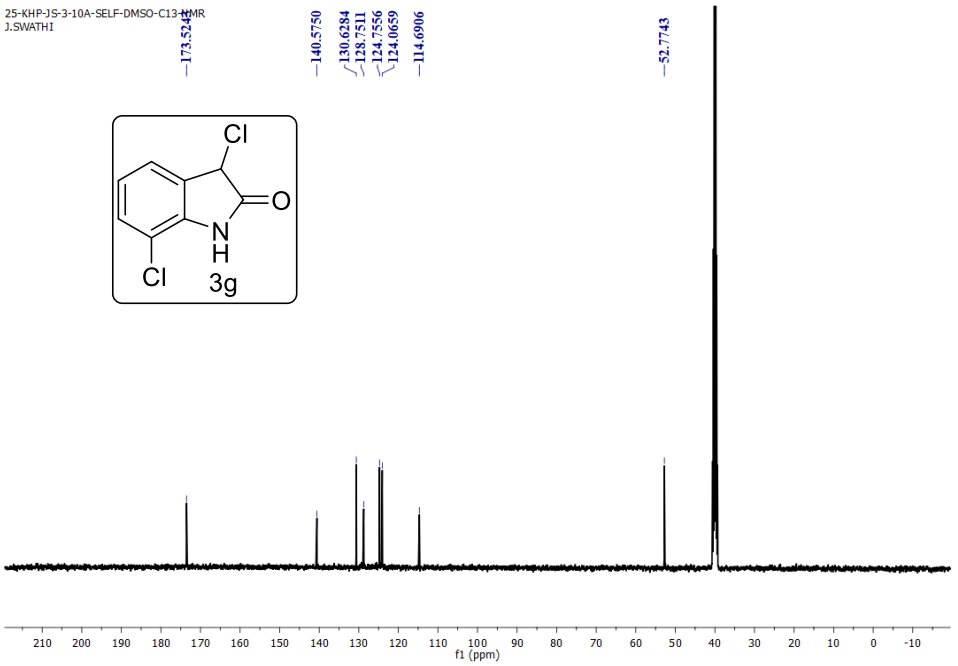
HRMS of 3,5-dichloroindolin-2-one (3f)



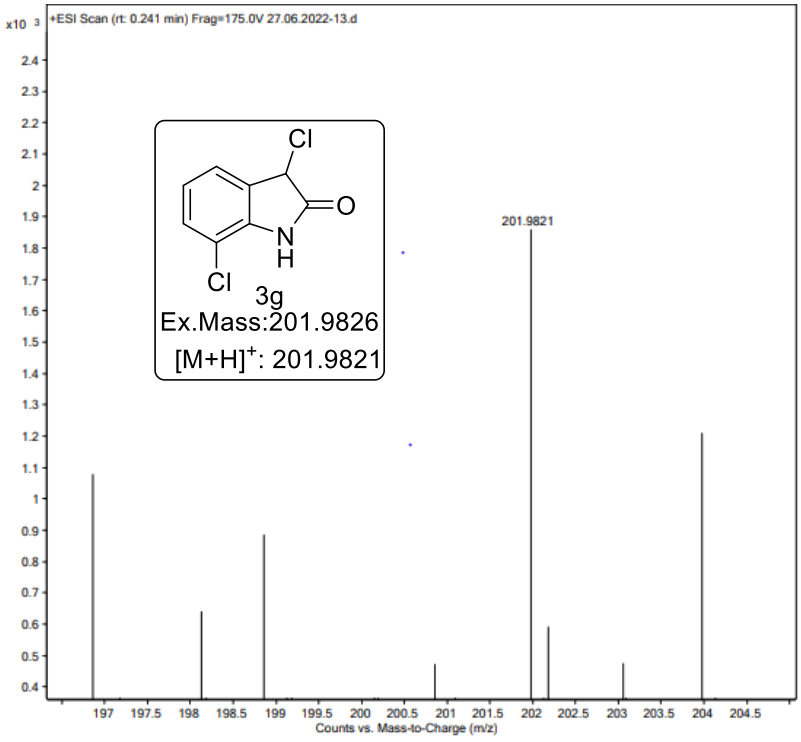
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 3,7-dichloroindolin-2-one (3g)



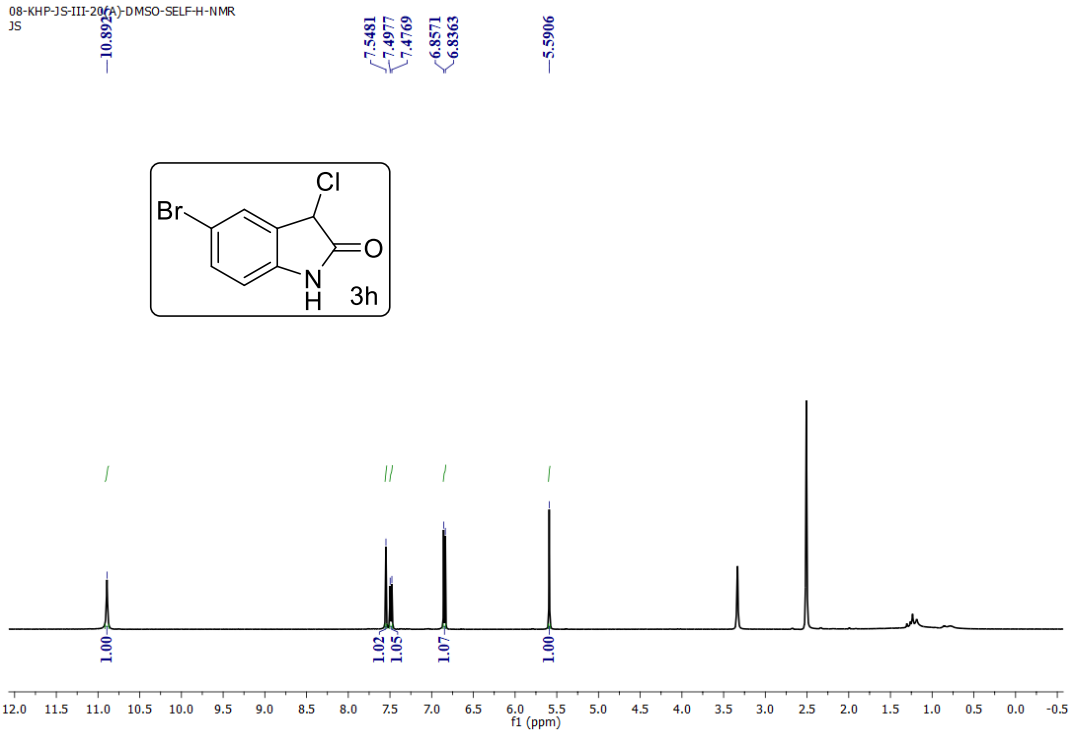
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of 3,7-dichloroindolin-2-one (3g)



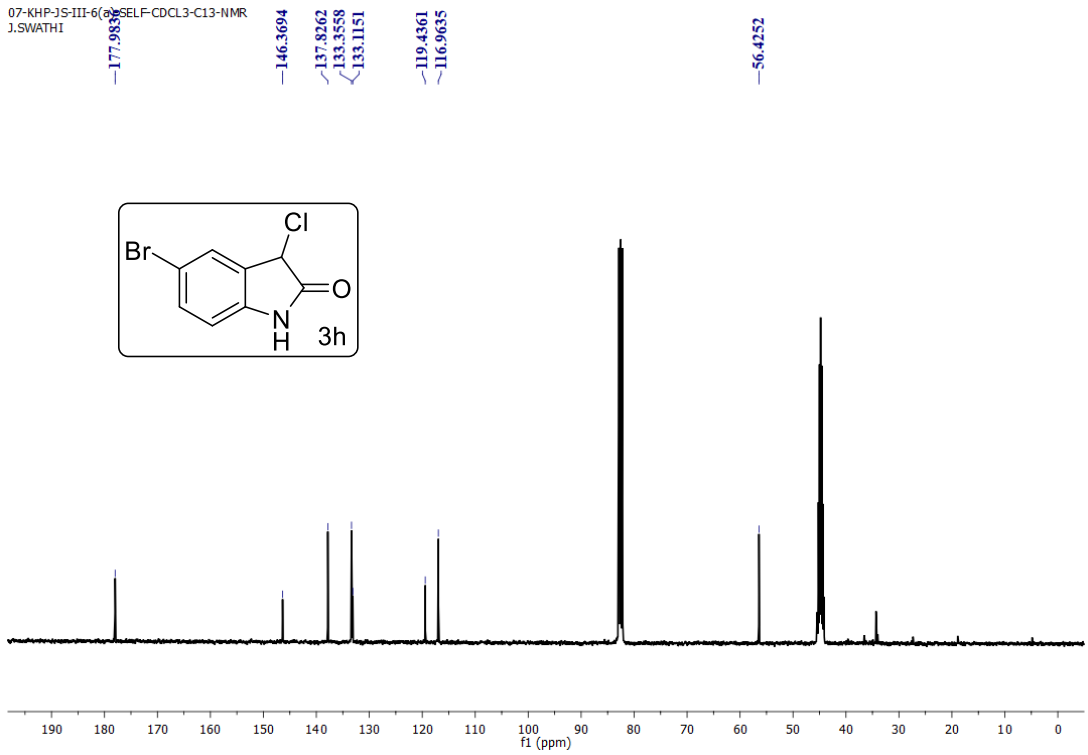
HRMS of 3,7-dichloroindolin-2-one (3g)



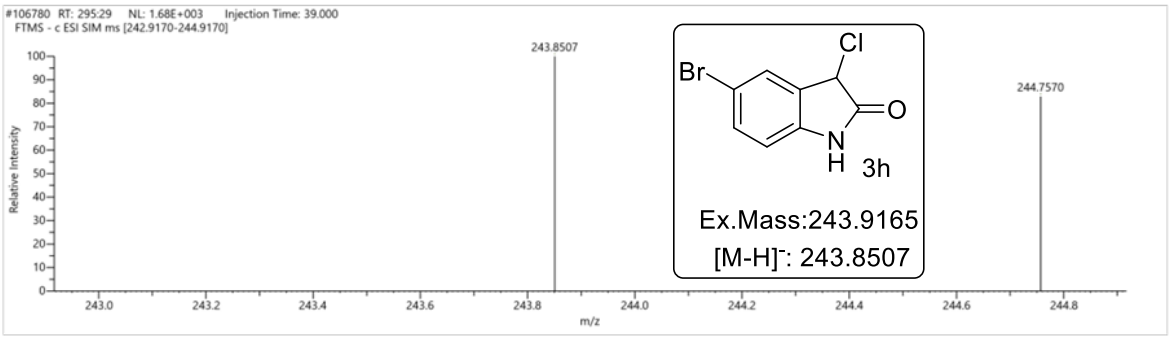
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 5-bromo-3-chloroindolin-2-one (3h)



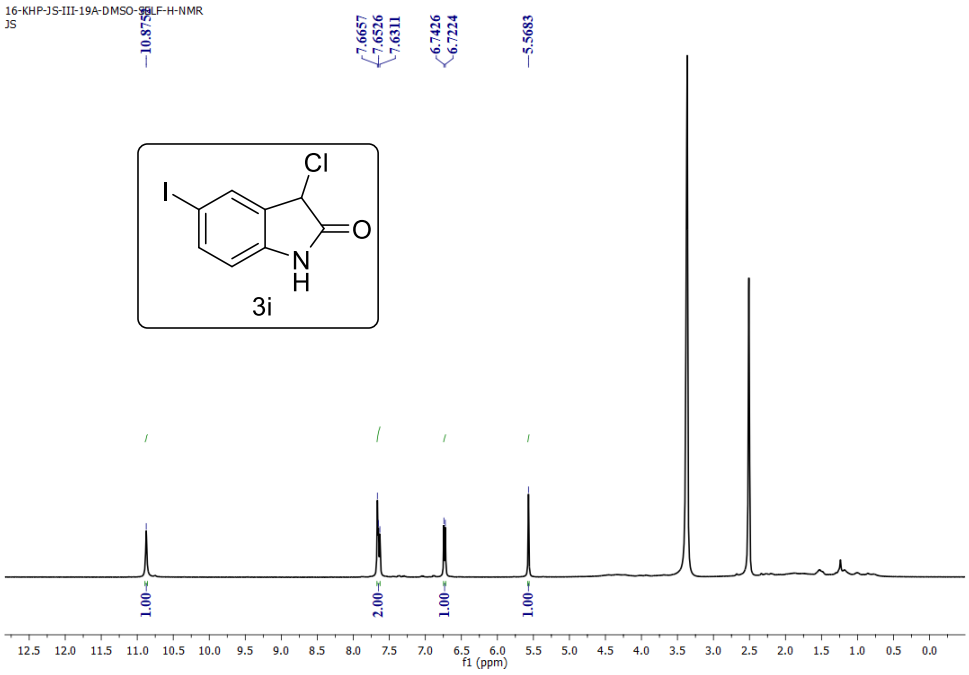
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6 + $CDCl_3$) spectrum of 5-bromo-3-chloroindolin-2-one (3h)



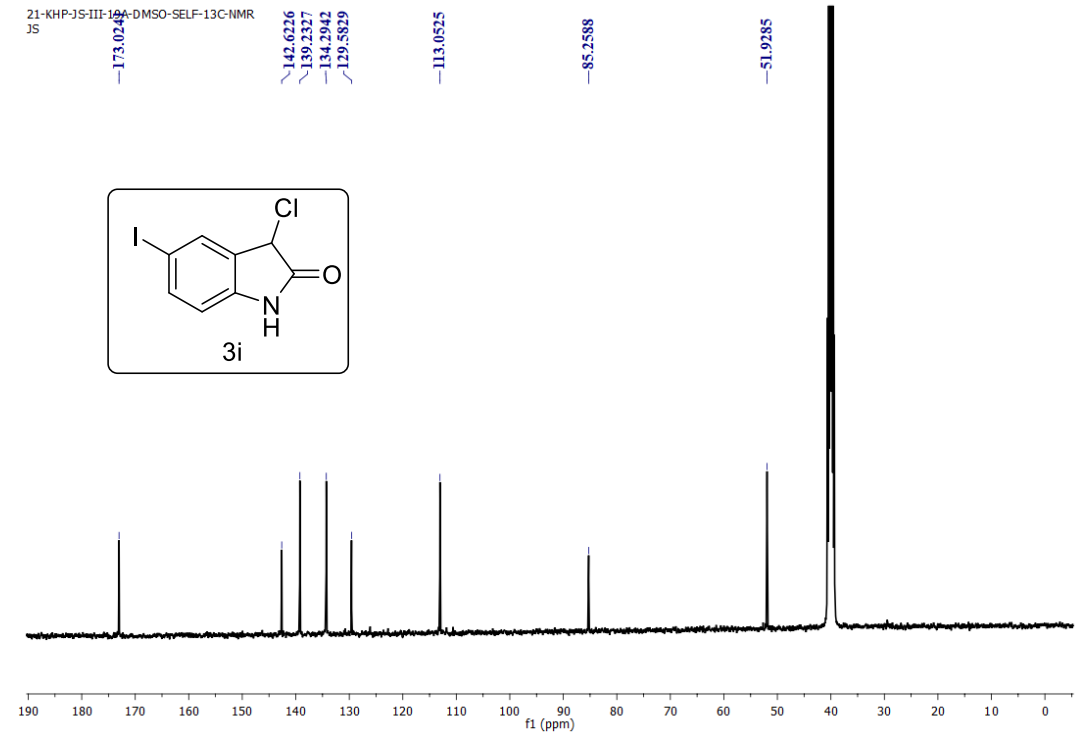
HRMS of 5-bromo-3-chloroindolin-2-one (3h)



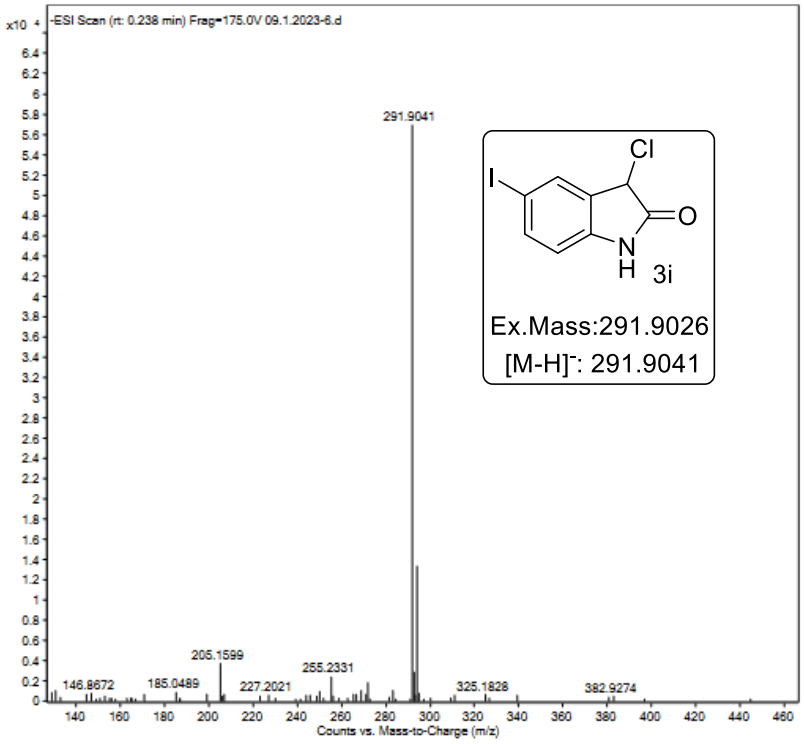
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 3-chloro-5-iodoindolin-2-one (3i)



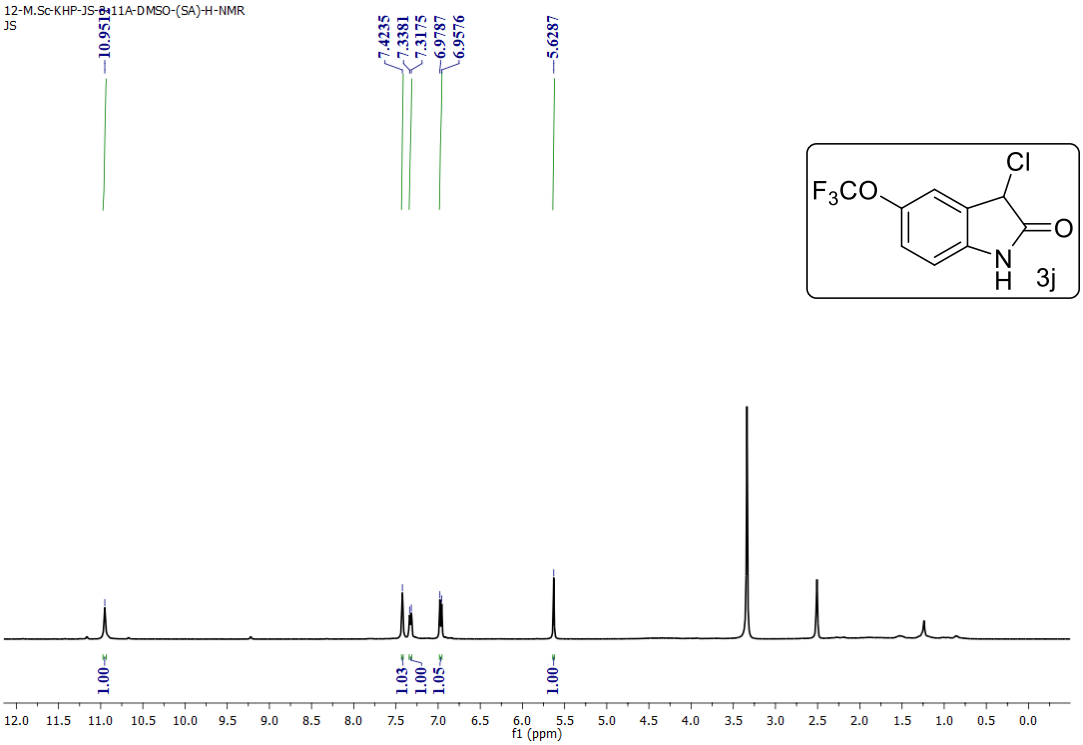
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of 3-chloro-5-iodoindolin-2-one (3i)



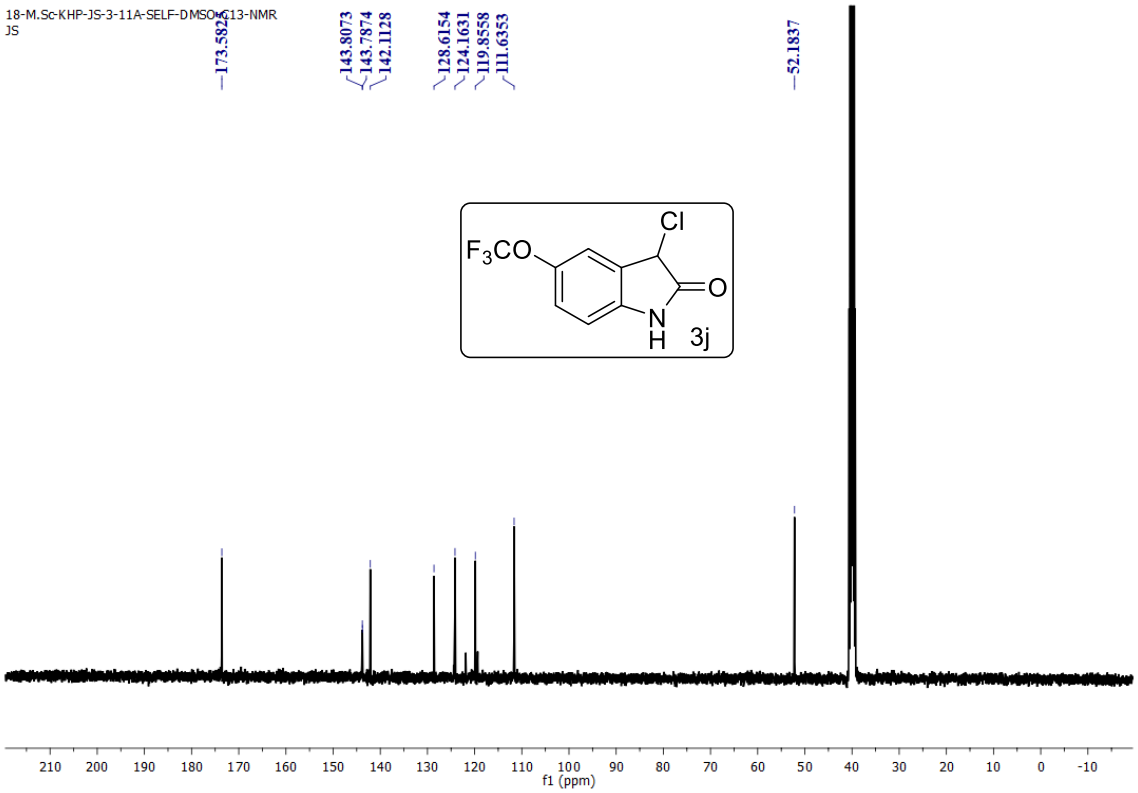
HRMS of 3-chloro-5-iodoindolin-2-one (3i)



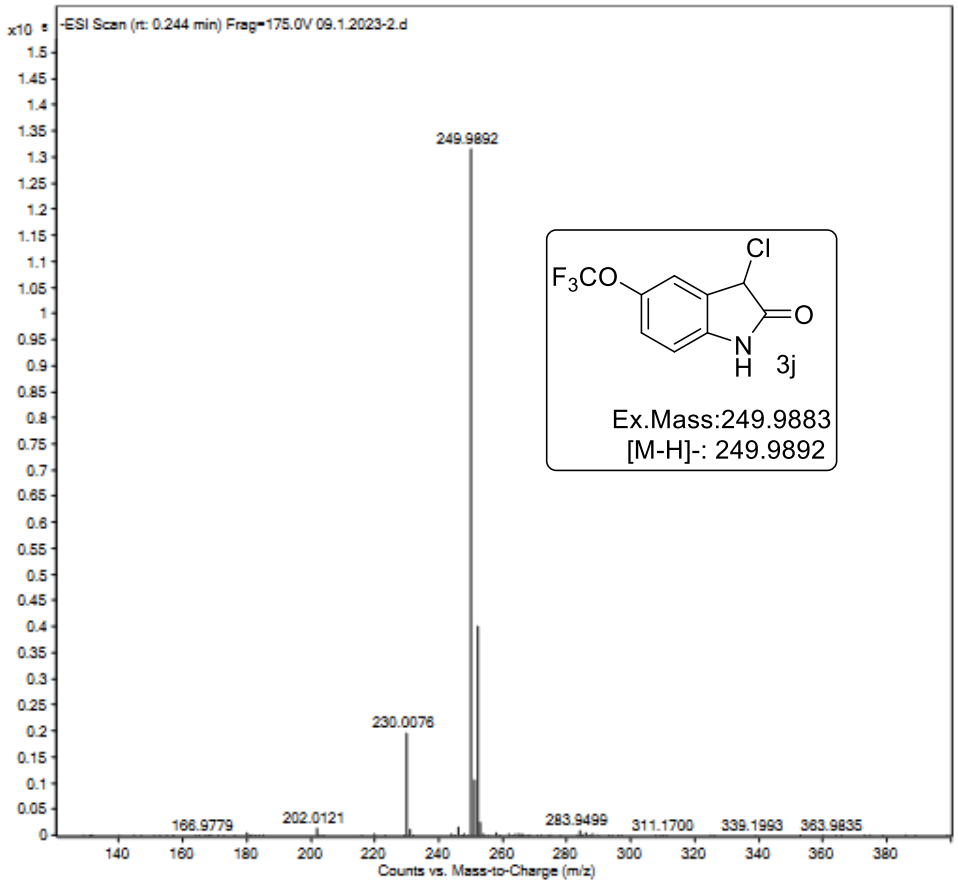
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 3-chloro-5-(trifluoromethoxy)indolin-2-one (3j)



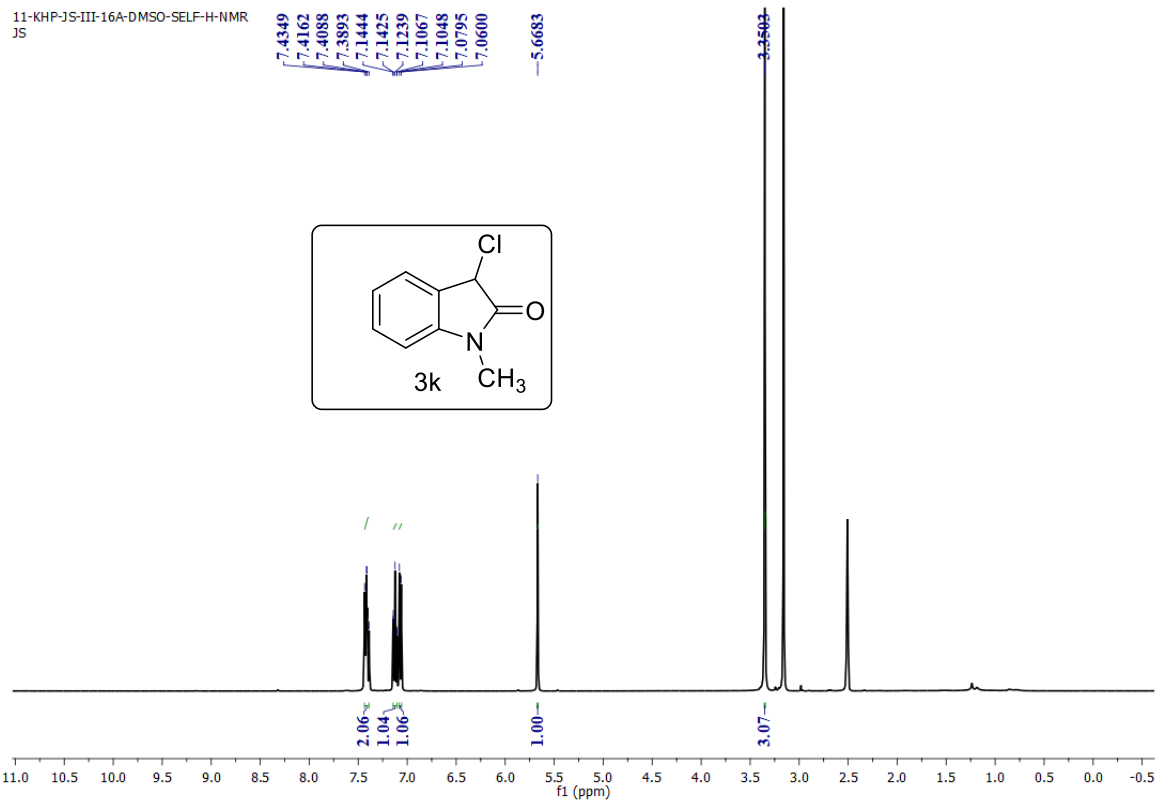
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of 3-chloro-5-(trifluoromethoxy)indolin-2-one (3j)



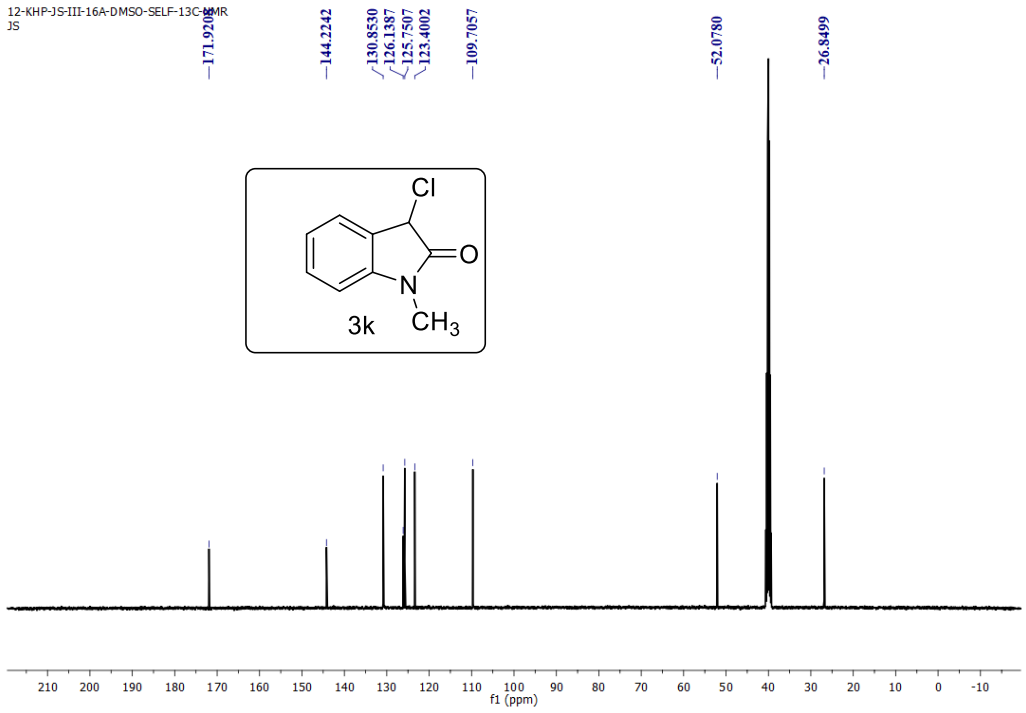
HRMS of 3-chloro-5-(trifluoromethoxy)indolin-2-one (3j)



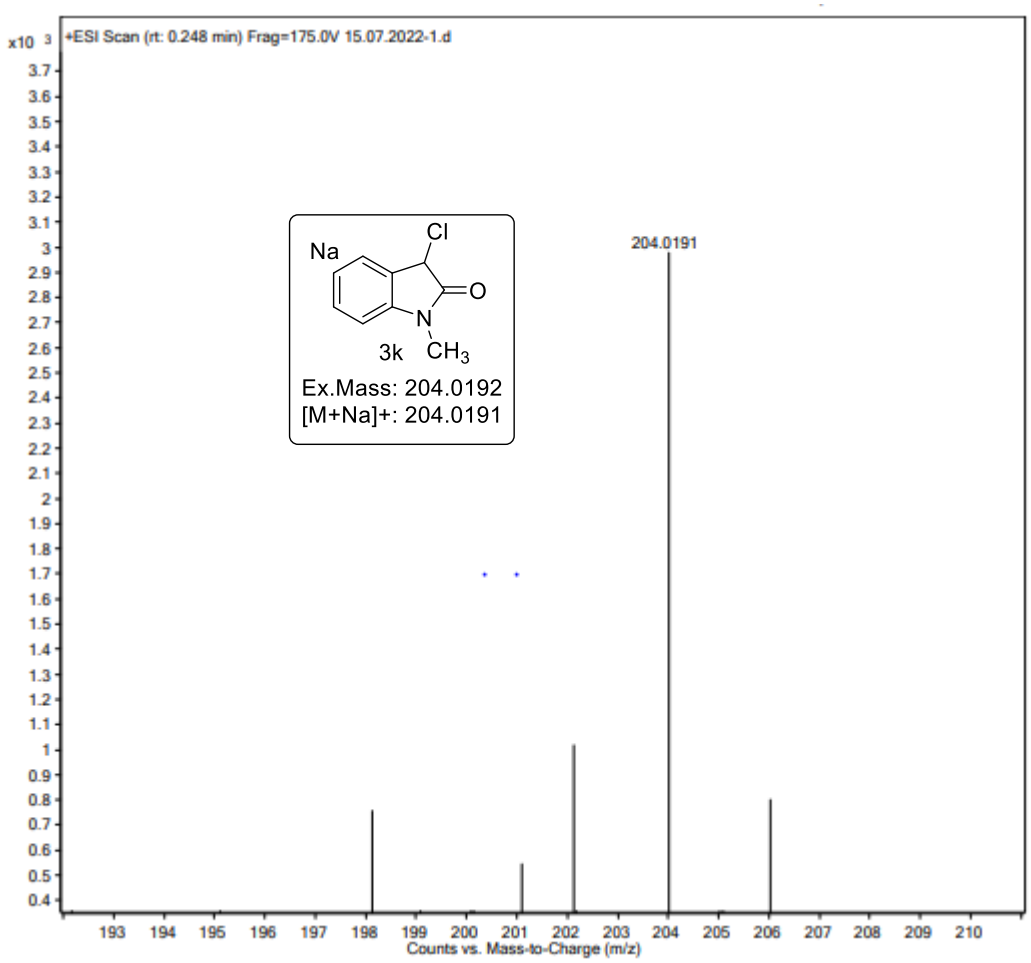
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 3-chloro-1-methylindolin-2-one (3k)



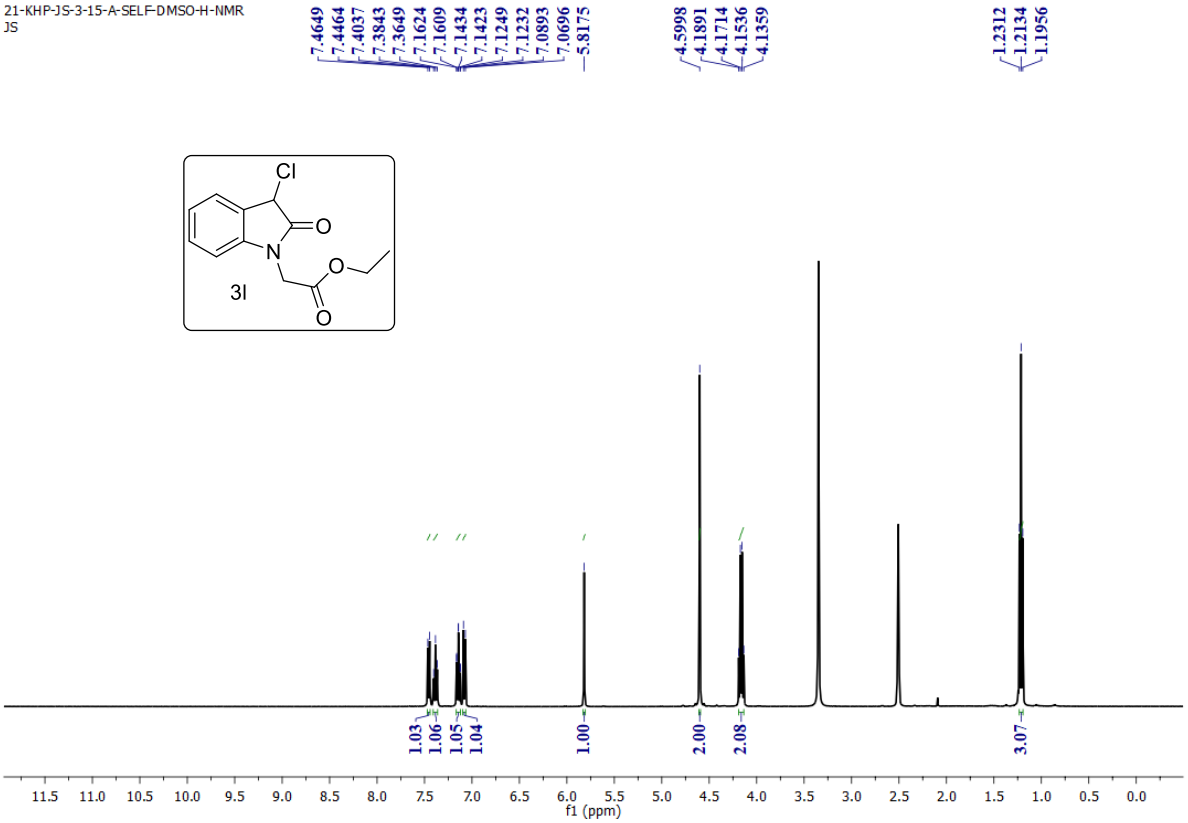
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of 3-chloro-1-methylindolin-2-one (3k)



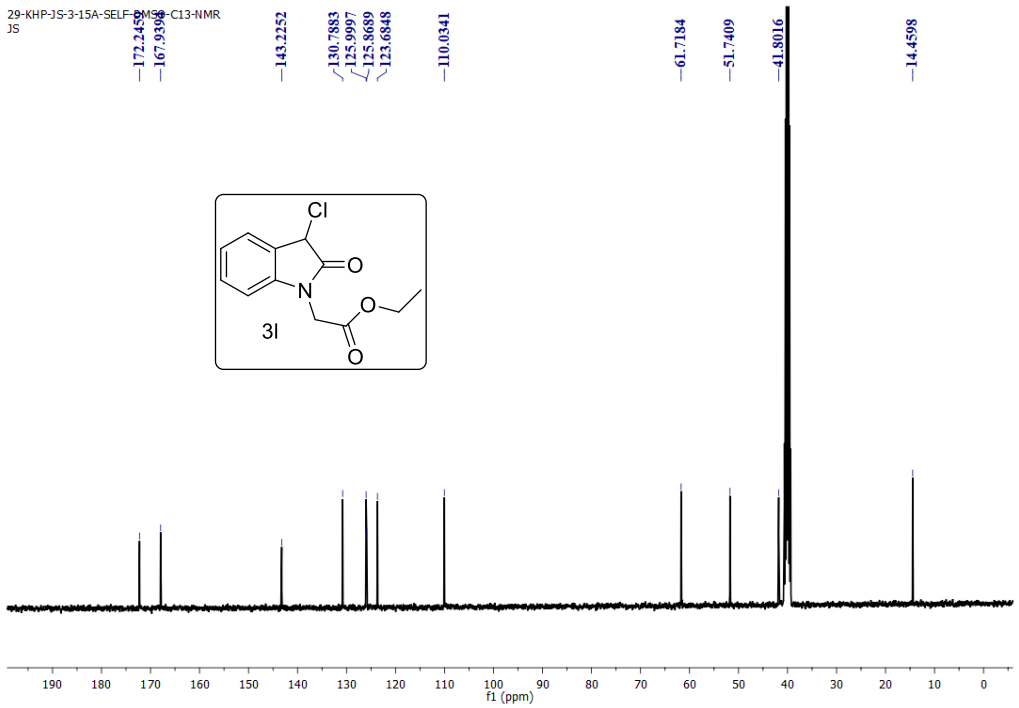
HRMS of 3-chloro-1-methylindolin-2-one (3k)



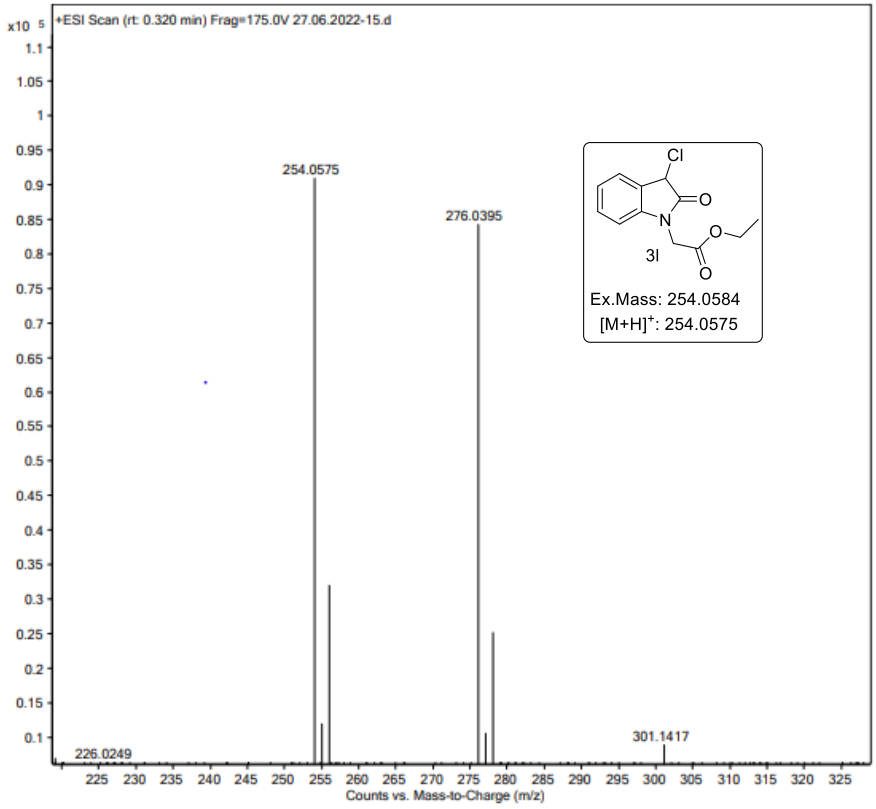
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of ethyl 2-(3-chloro-2-oxoindolin-1-yl)acetate (3l)



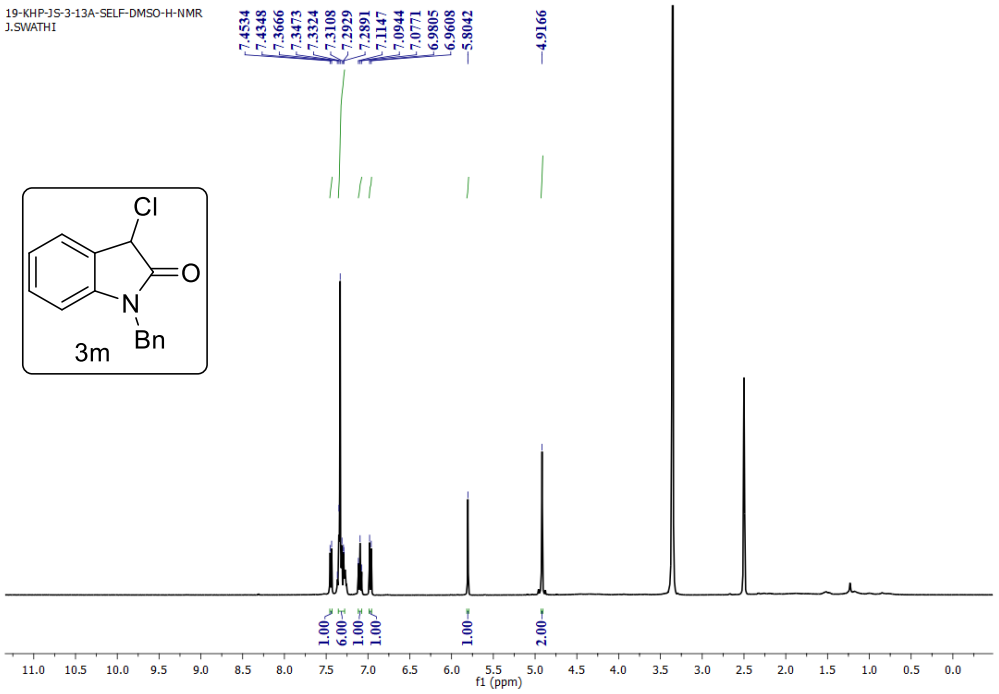
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of ethyl 2-(3-chloro-2-oxoindolin-1-yl)acetate (3l)



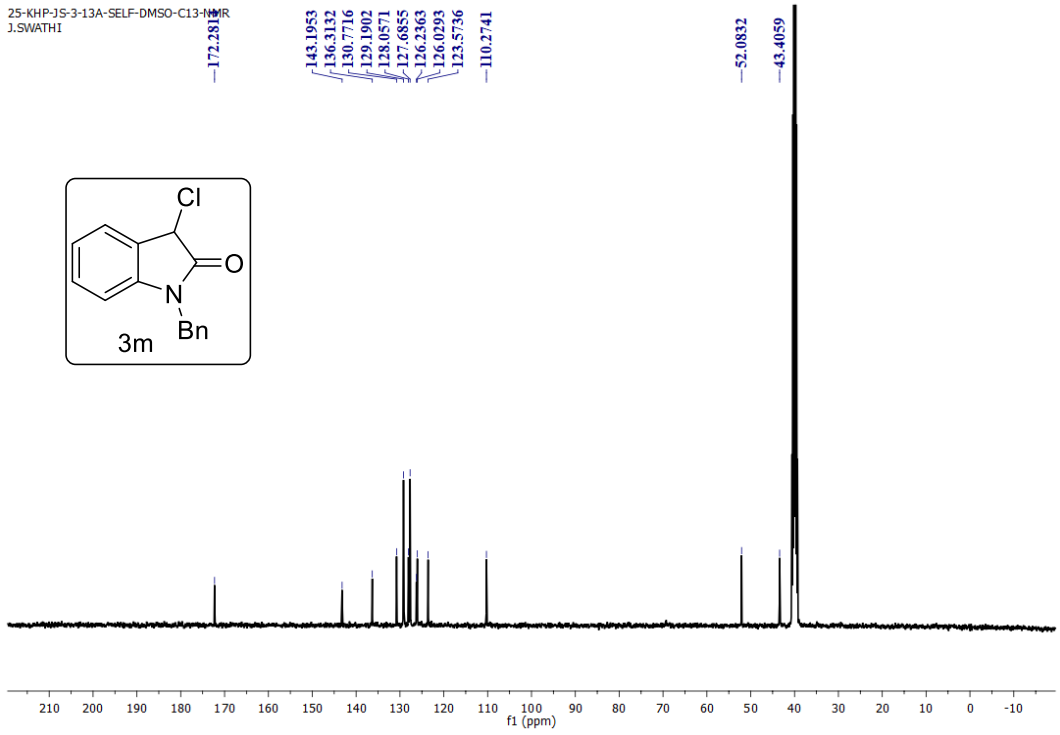
HRMS of ethyl 2-(3-chloro-2-oxoindolin-1-yl)acetate (3l)



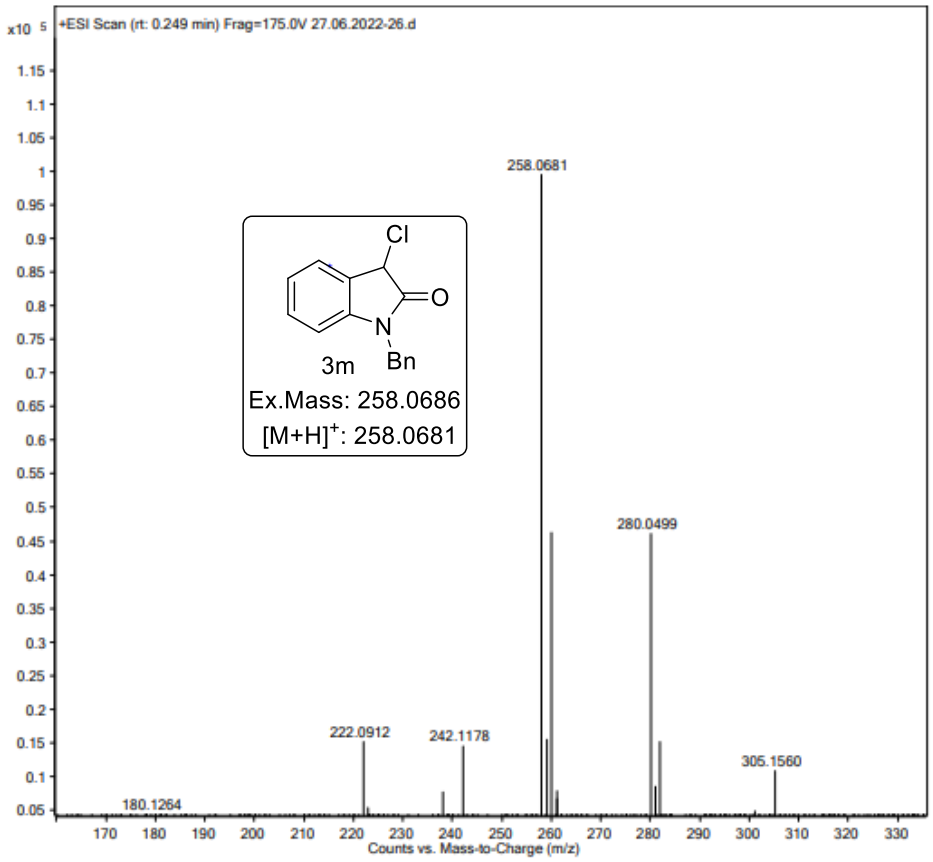
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 1-benzyl-3-chloroindolin-2-one (3m)



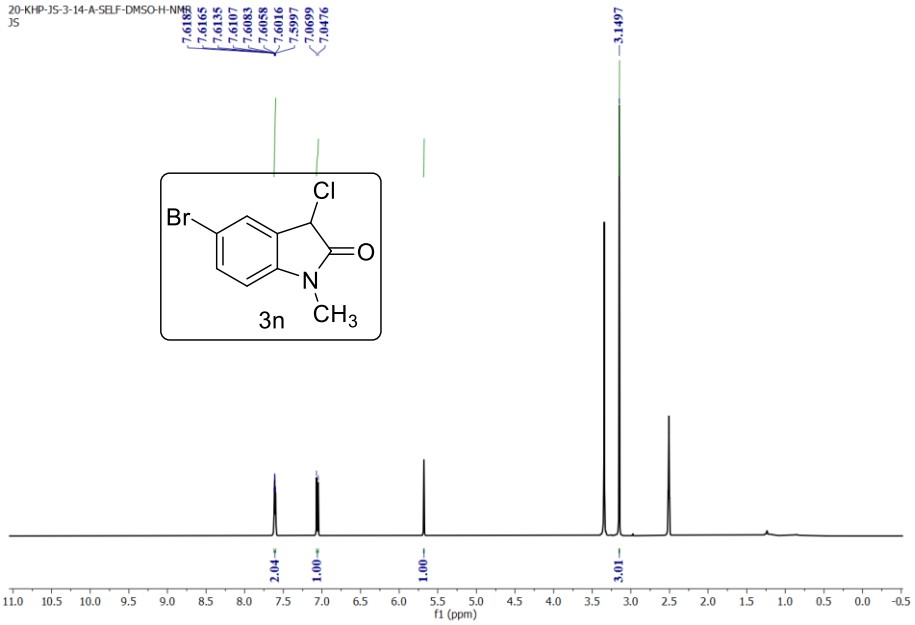
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of 1-benzyl-3-chloroindolin-2-one (3m)



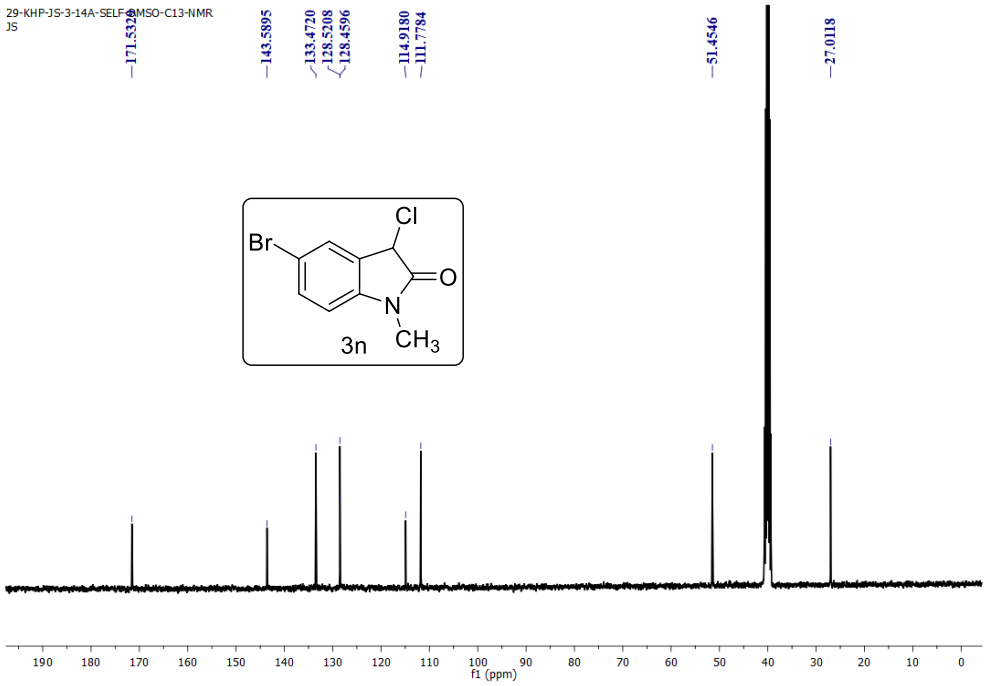
HRMS of 1-benzyl-3-chloroindolin-2-one (3m)



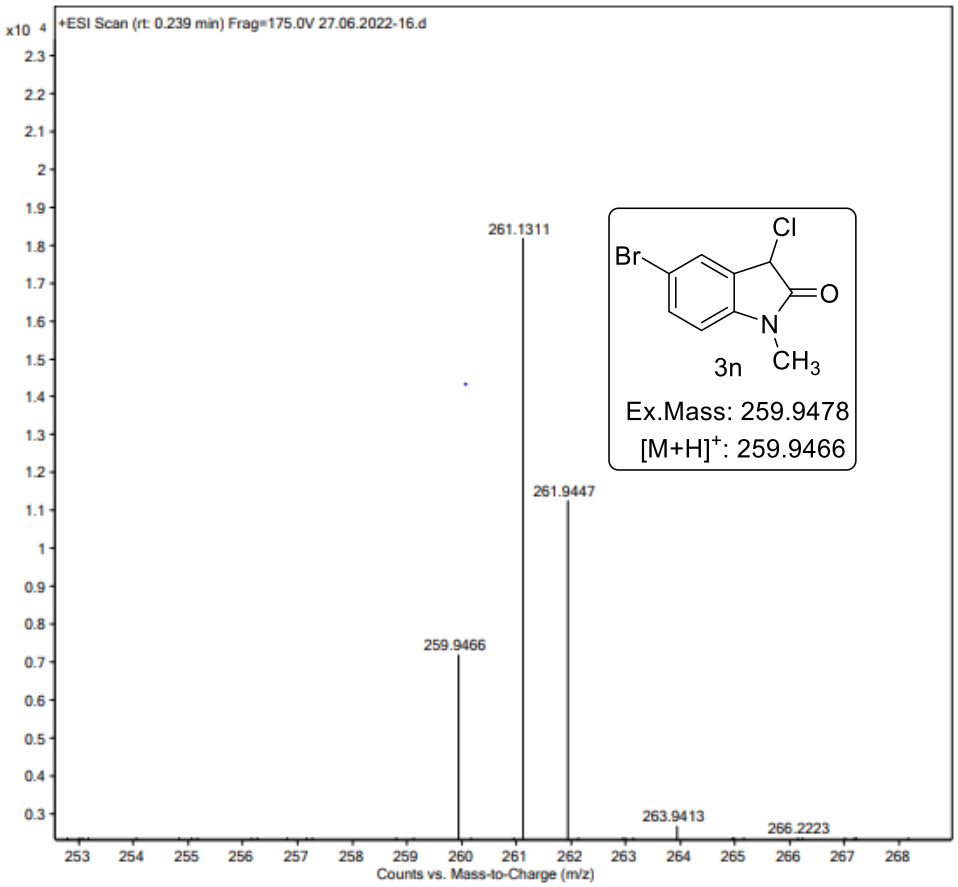
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 5-bromo-3-chloro-1-methylindolin-2-one (3n)



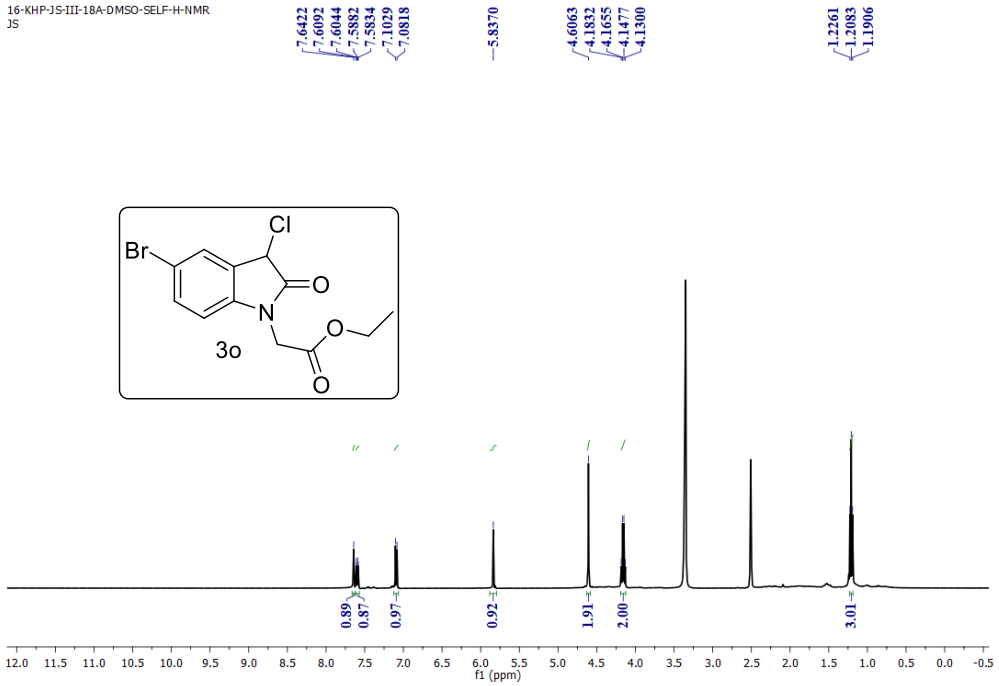
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of 5-bromo-3-chloro-1-methylindolin-2-one (3n)



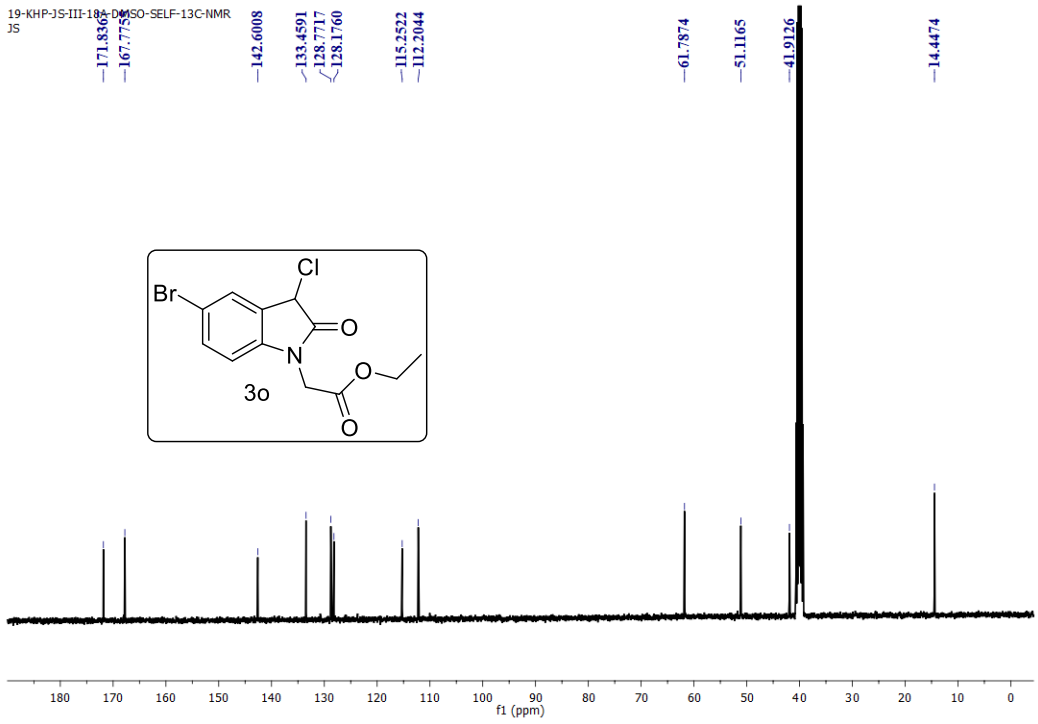
HRMS of 5-bromo-3-chloro-1-methylindolin-2-one (3n)



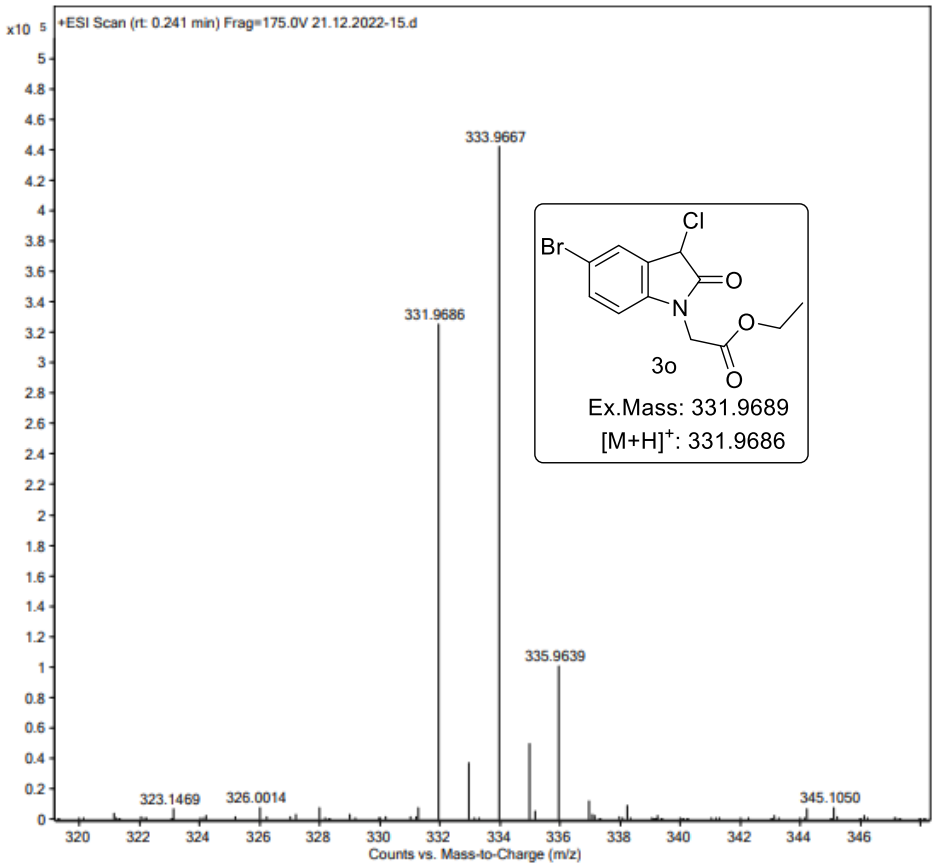
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of ethyl 2-(5-bromo-3-chloro-2-oxoindolin-1-yl)acetate (3o)



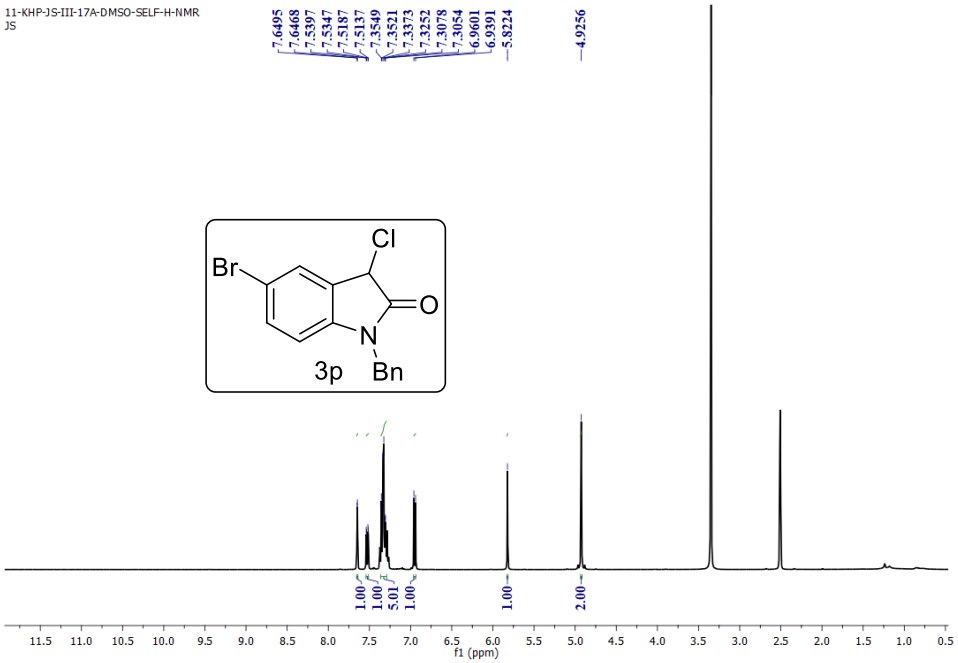
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of ethyl 2-(5-bromo-3-chloro-2-oxoindolin-1-yl)acetate (3o)



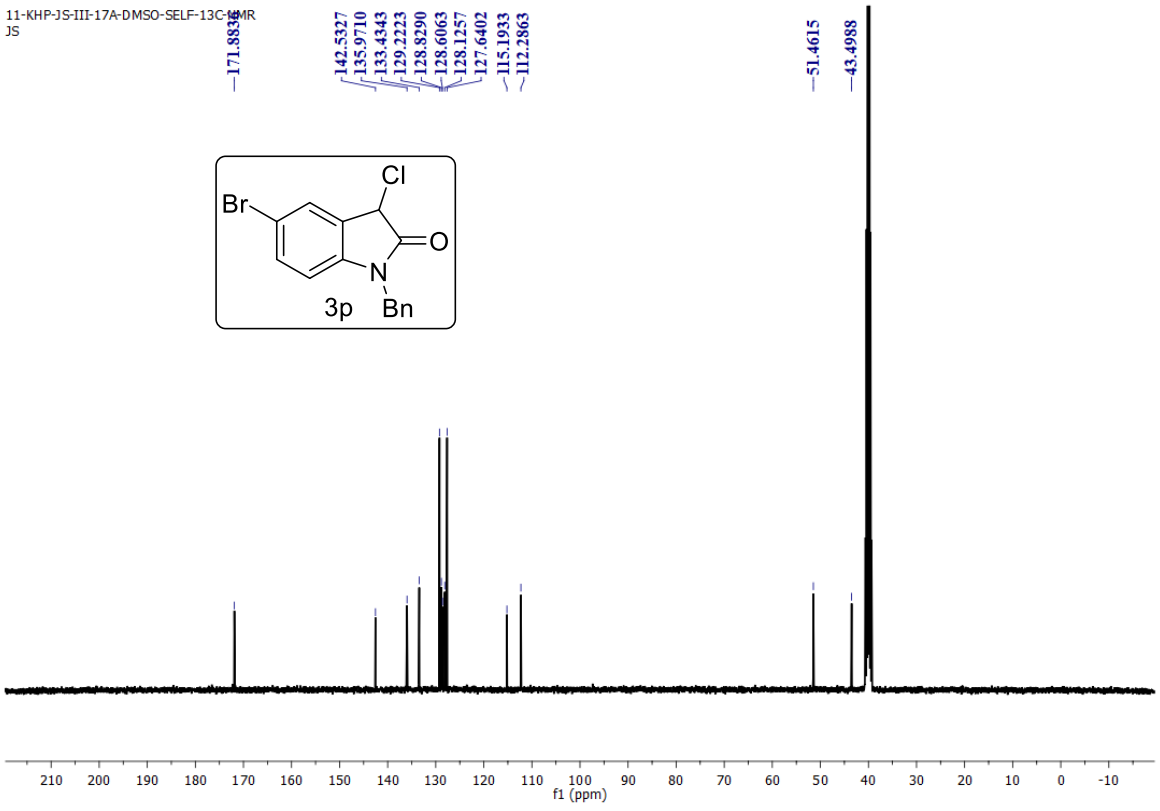
HRMS of ethyl 2-(5-bromo-3-chloro-2-oxoindolin-1-yl)acetate (3o)



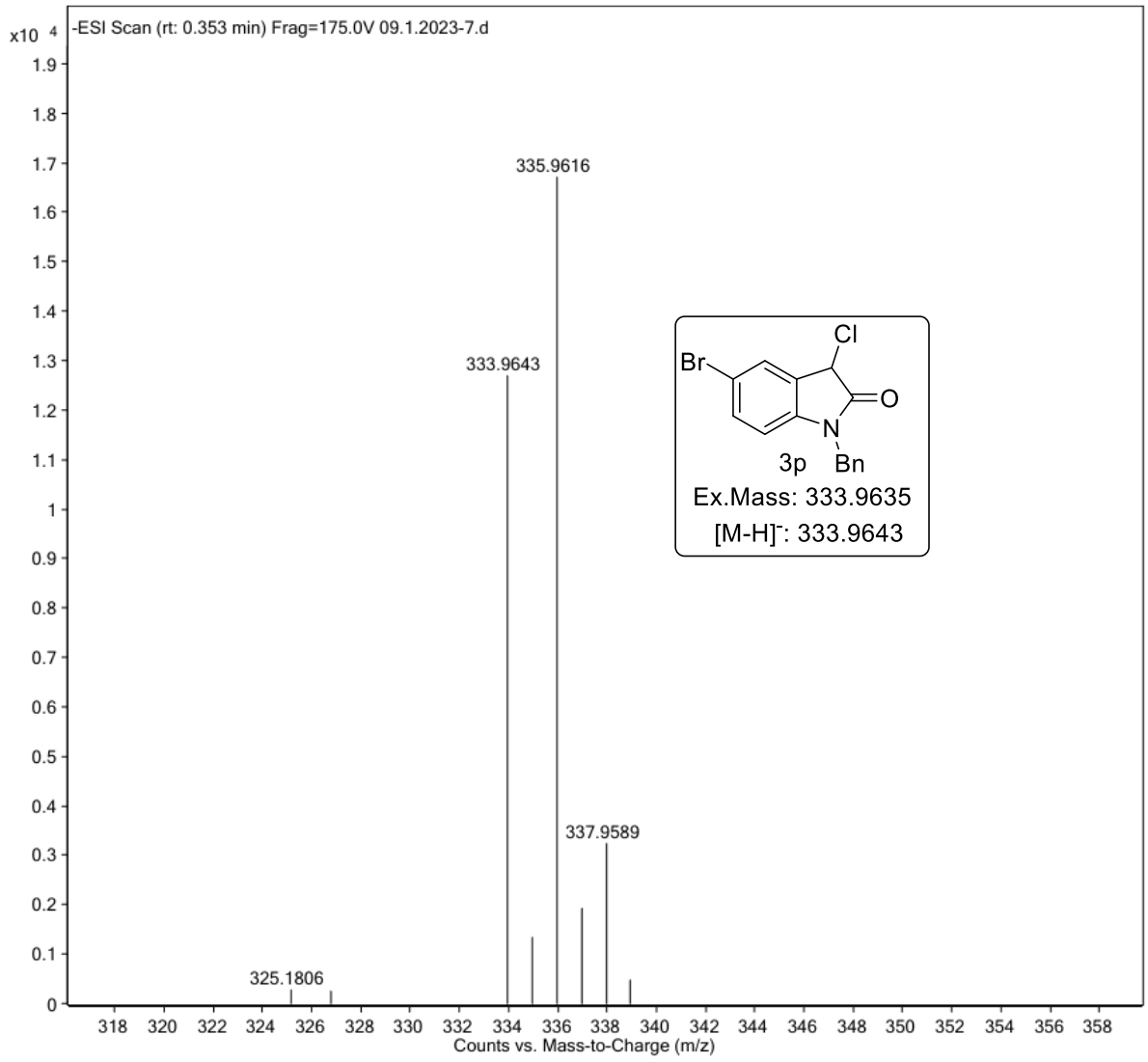
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 1-benzyl-5-bromo-3-chloroindolin-2-one (3p)



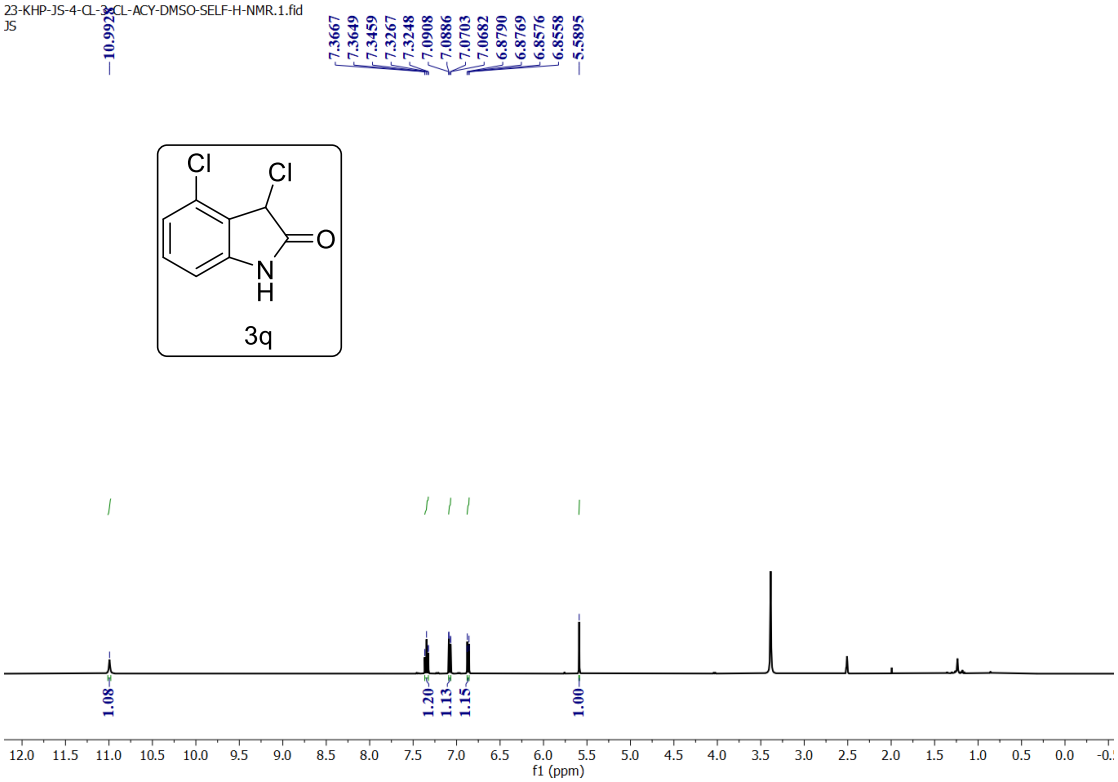
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of 1-benzyl-5-bromo-3-chloroindolin-2-one (3p)



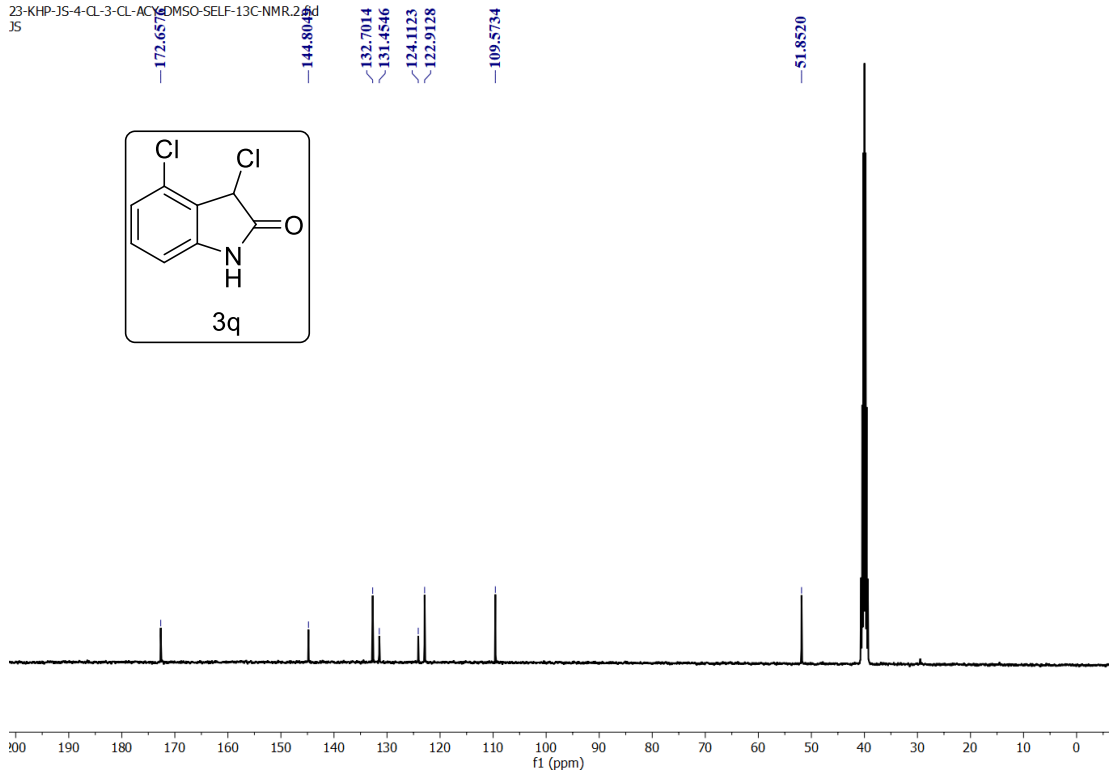
HRMS of 1-benzyl-5-bromo-3-chloroindolin-2-one (3p)



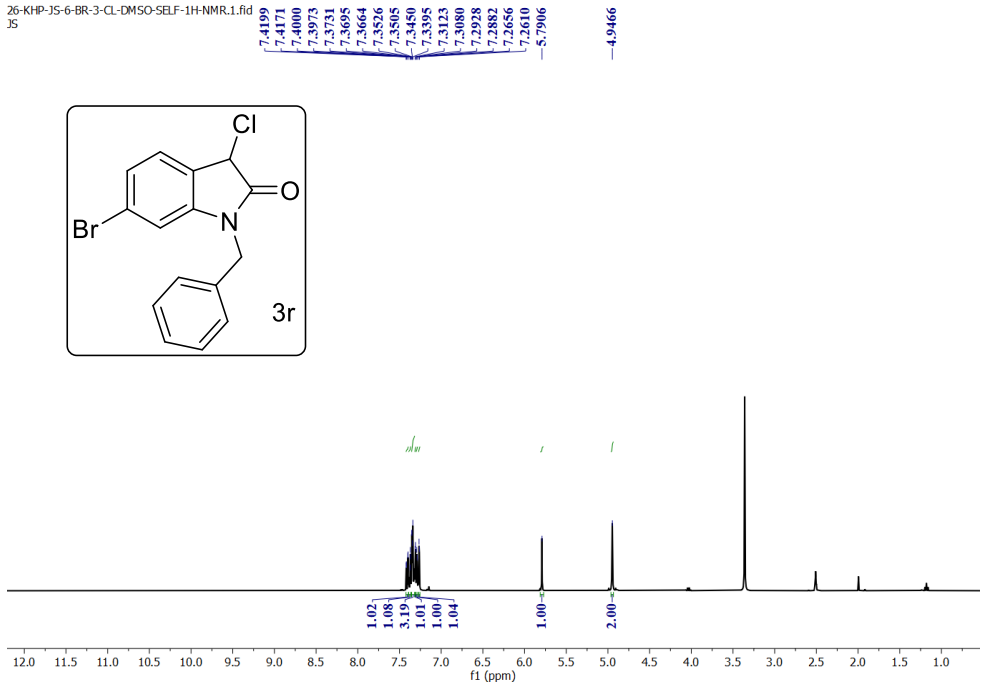
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 4-Chloroindolin-2-one (3q)



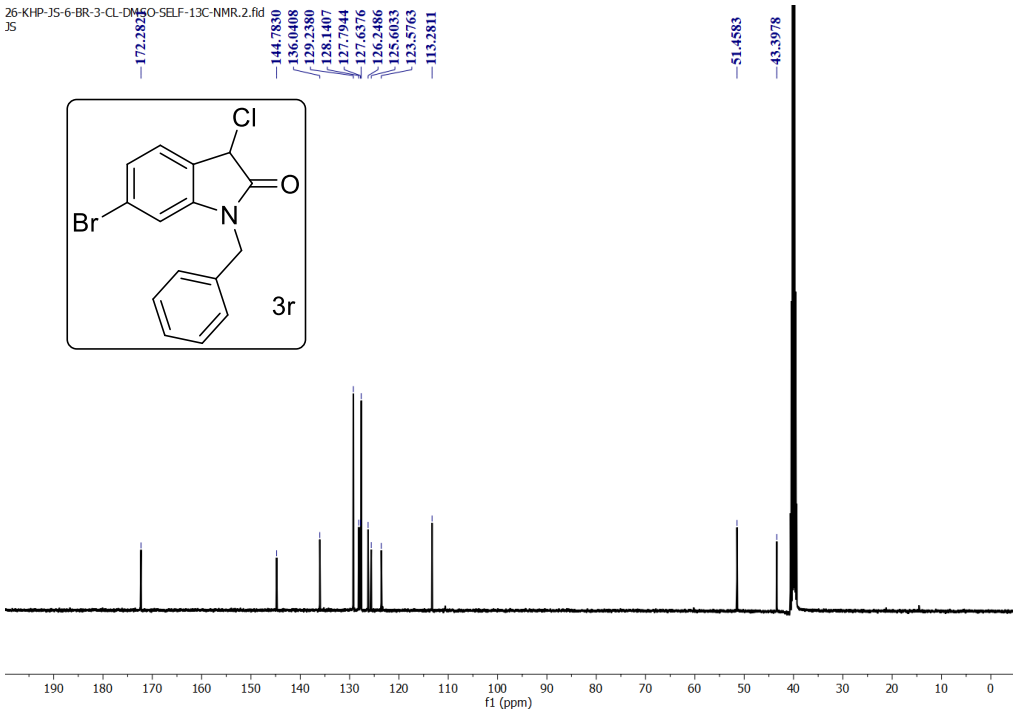
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of 4-Chloroindolin-2-one (3q)



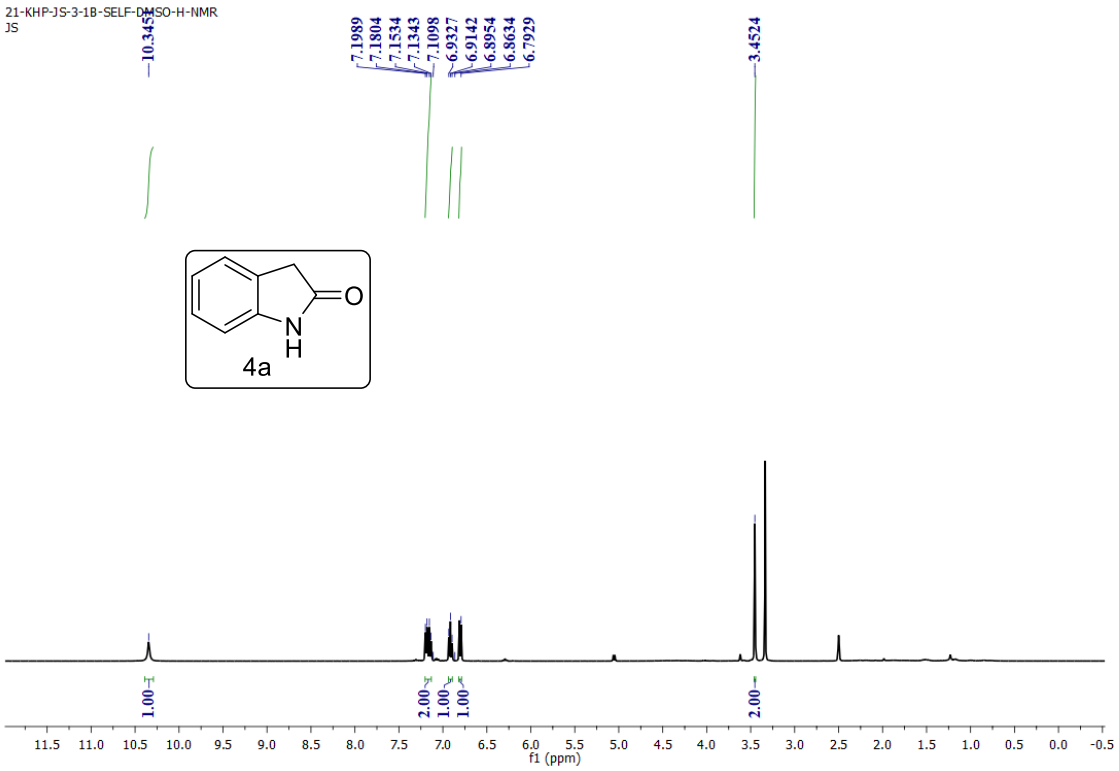
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 1-benzyl-6-bromoindolin-2-one(3r)



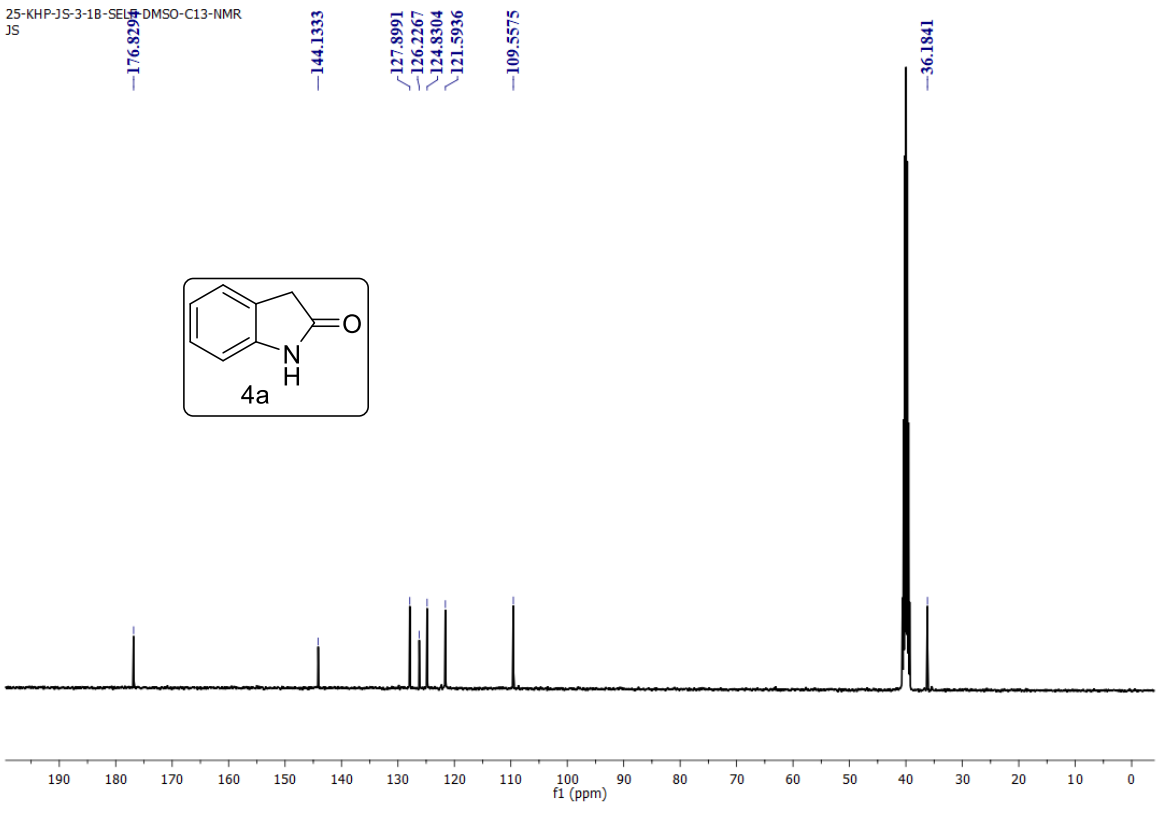
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) spectrum 1-benzyl-6-bromoindolin-2-one(3r)



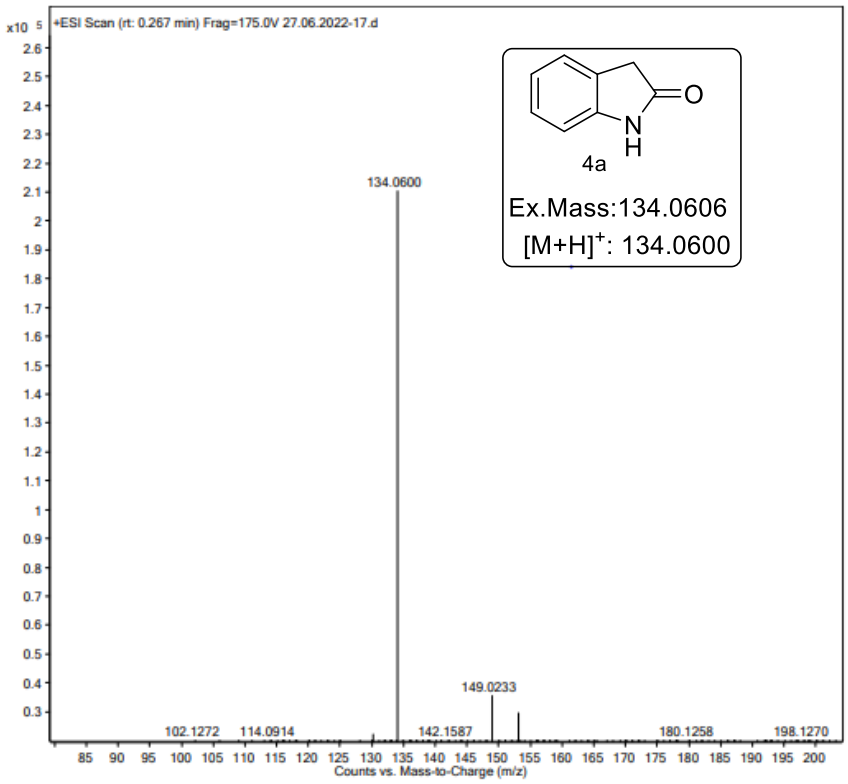
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of indolin-2-one (4a)



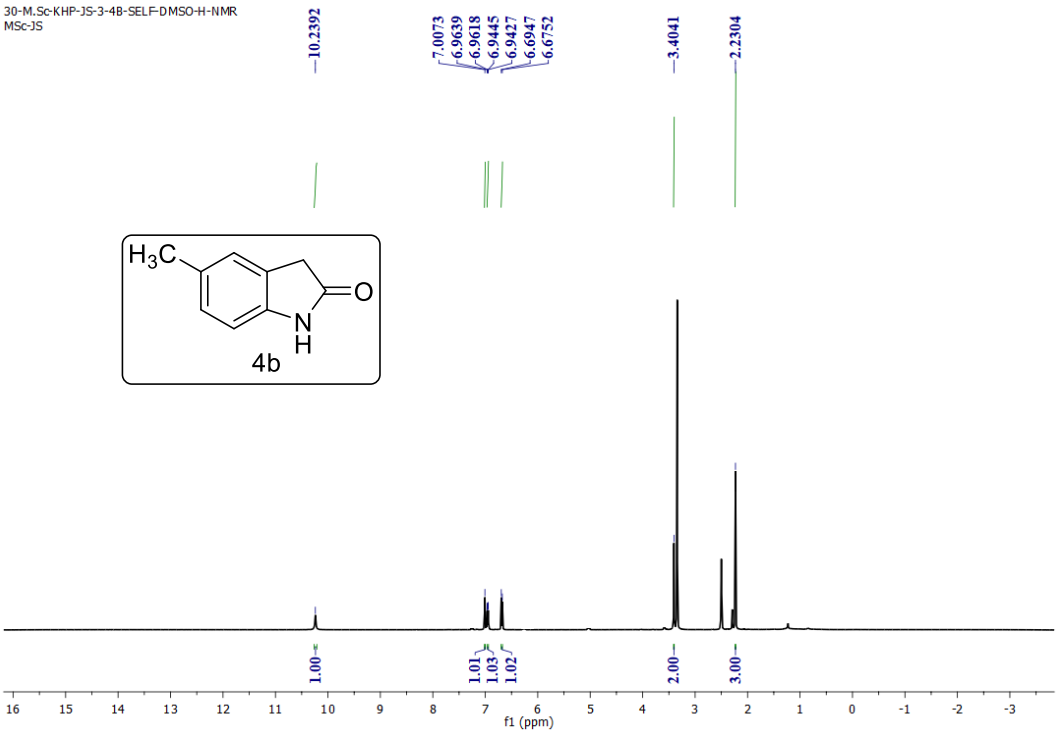
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of indolin-2-one (4a)



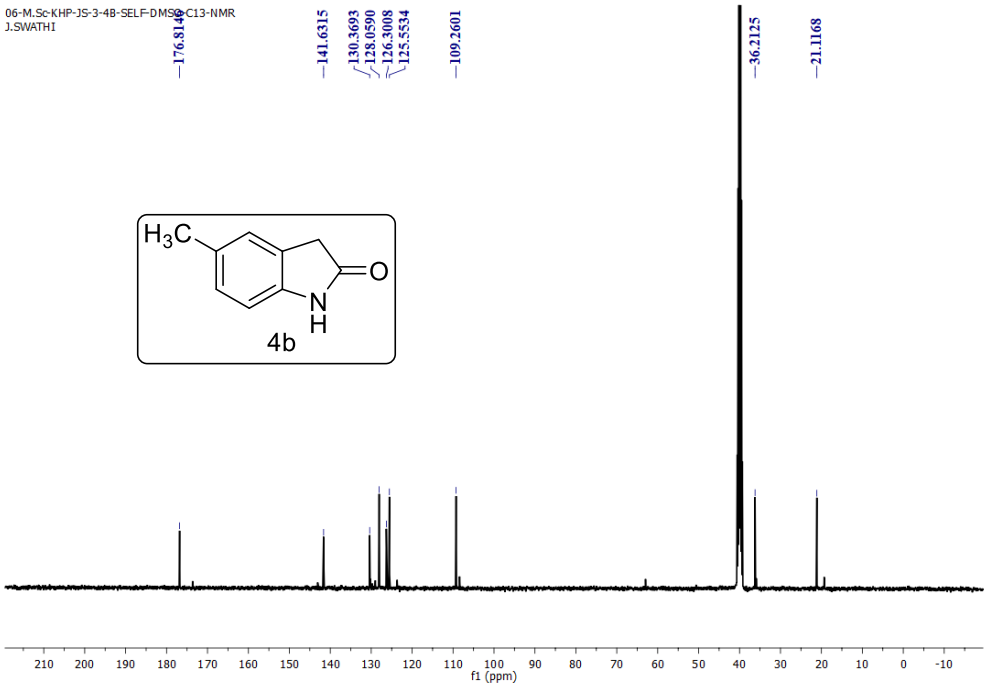
HRMS of indolin-2-one (4a)



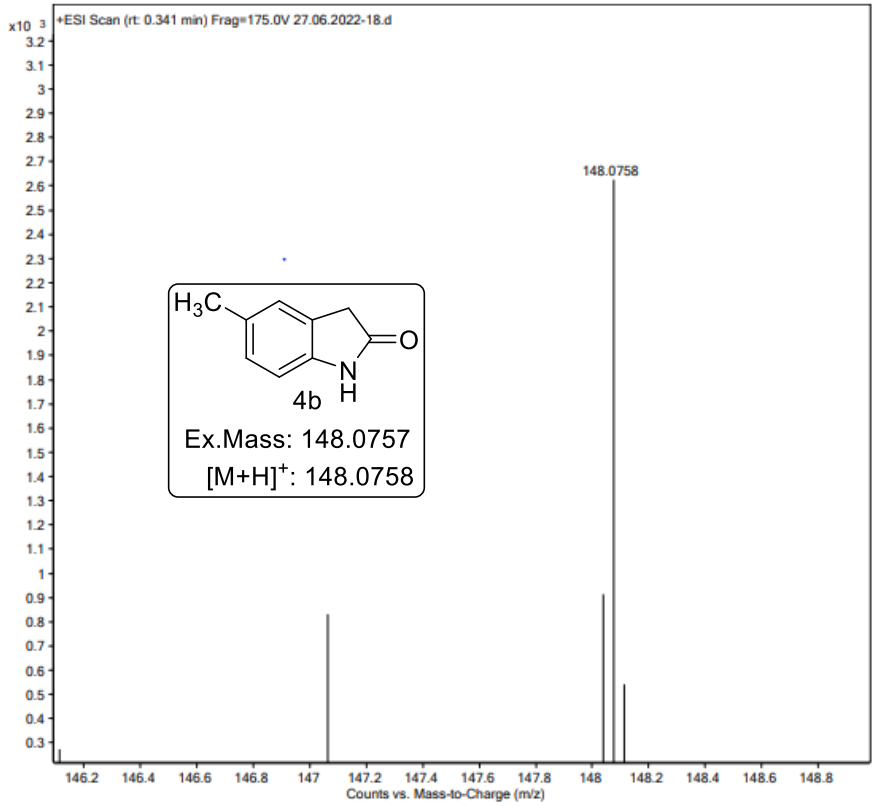
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 5-methylindolin-2-one (4b)



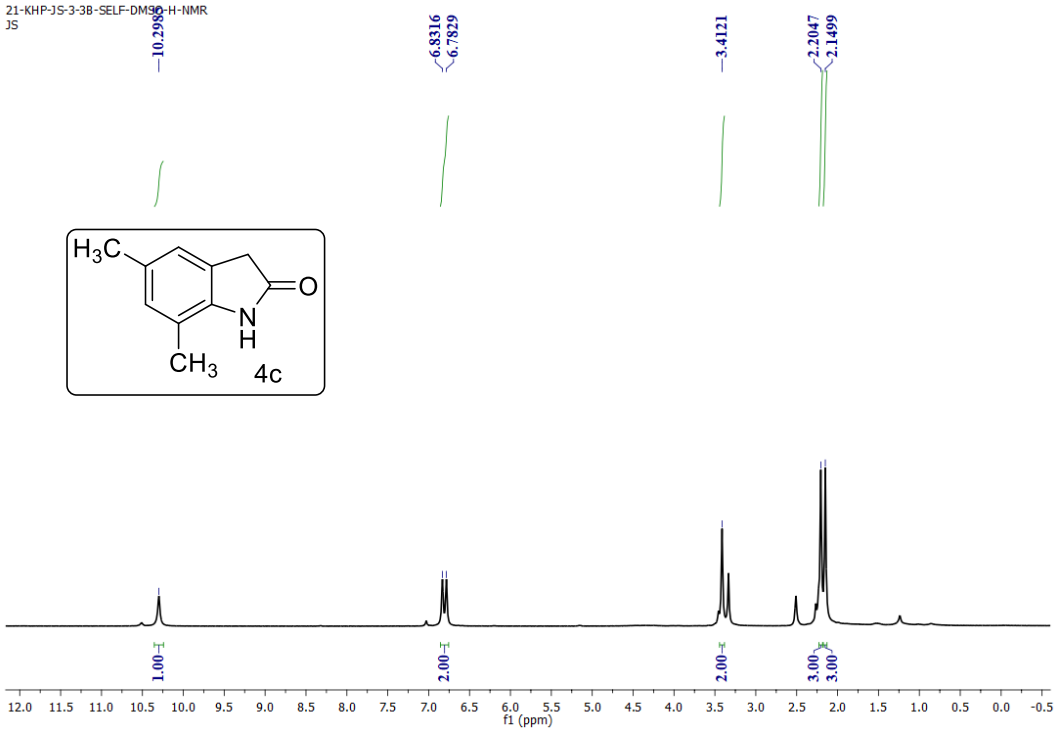
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of 5-methylindolin-2-one (4b)



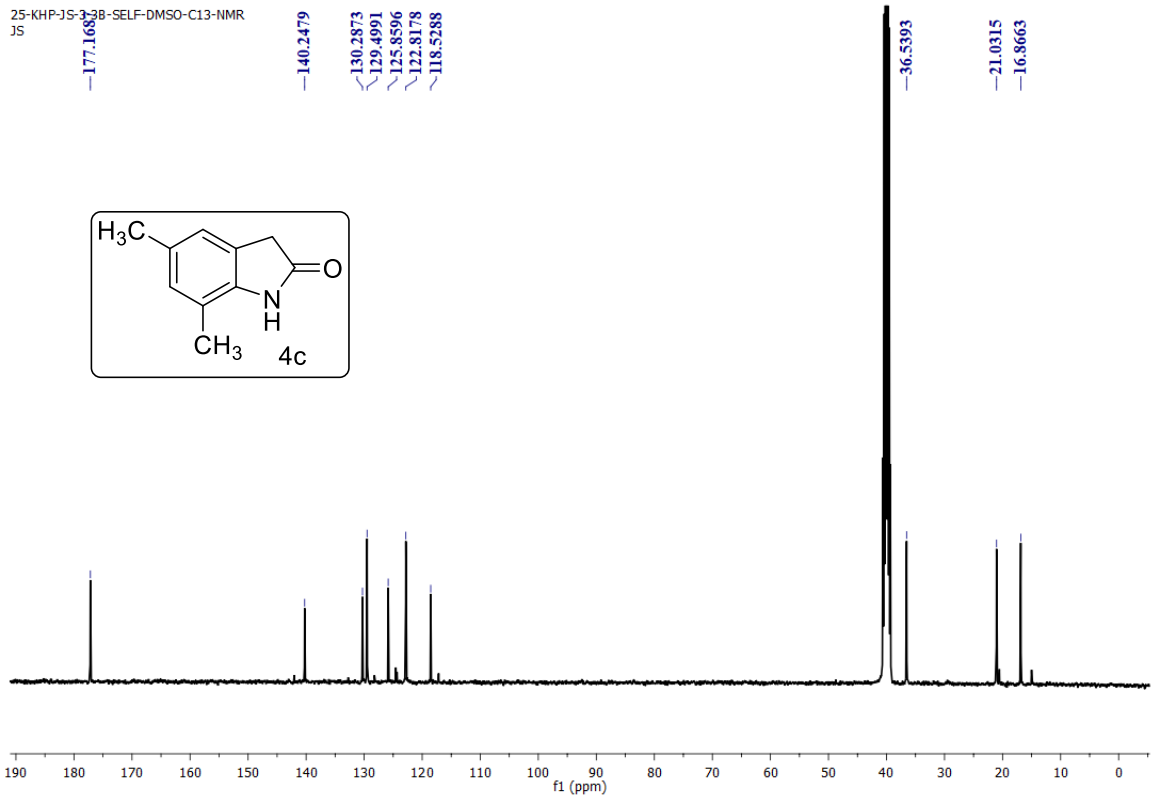
HRMS of 5-methylindolin-2-one (4b)



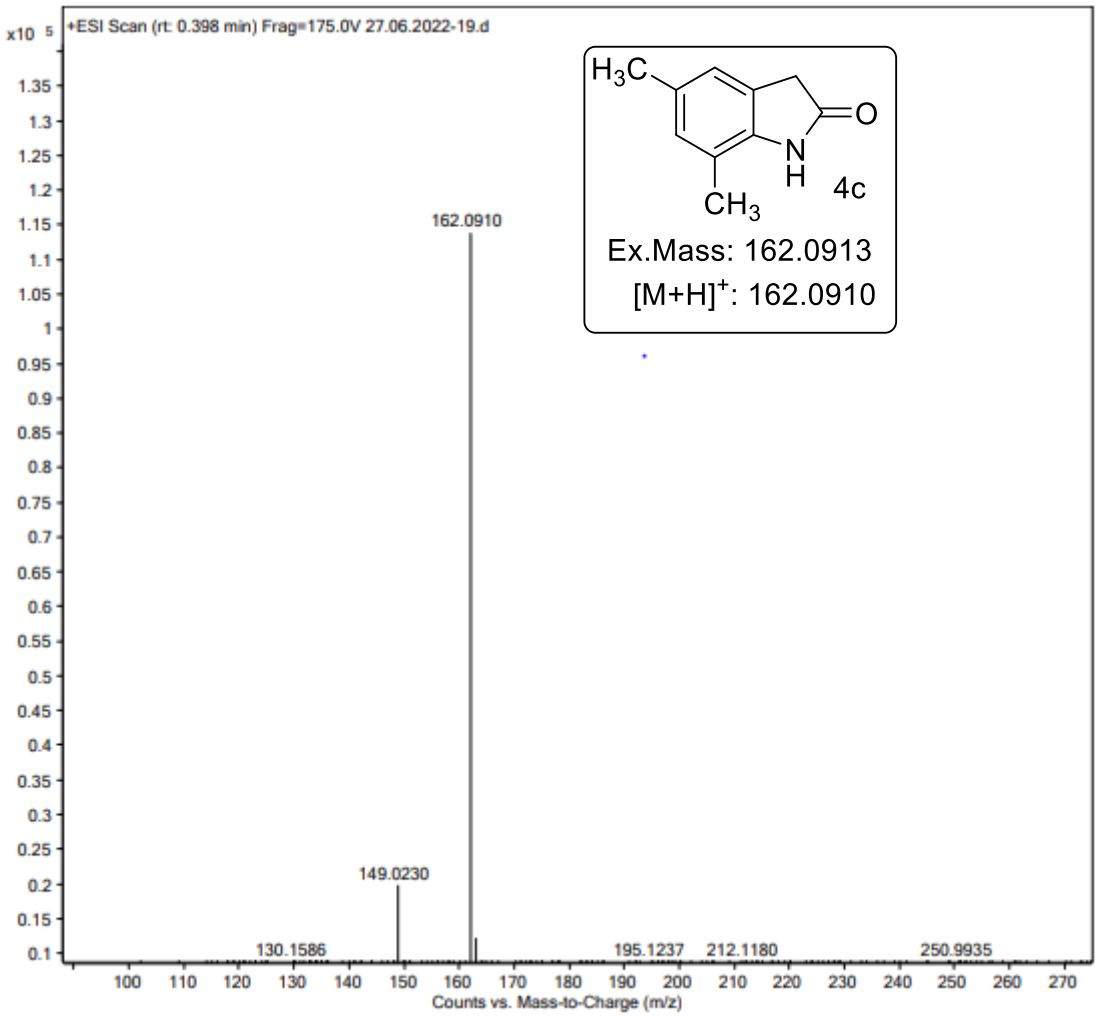
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 5,7-dimethylindolin-2-one (4c)



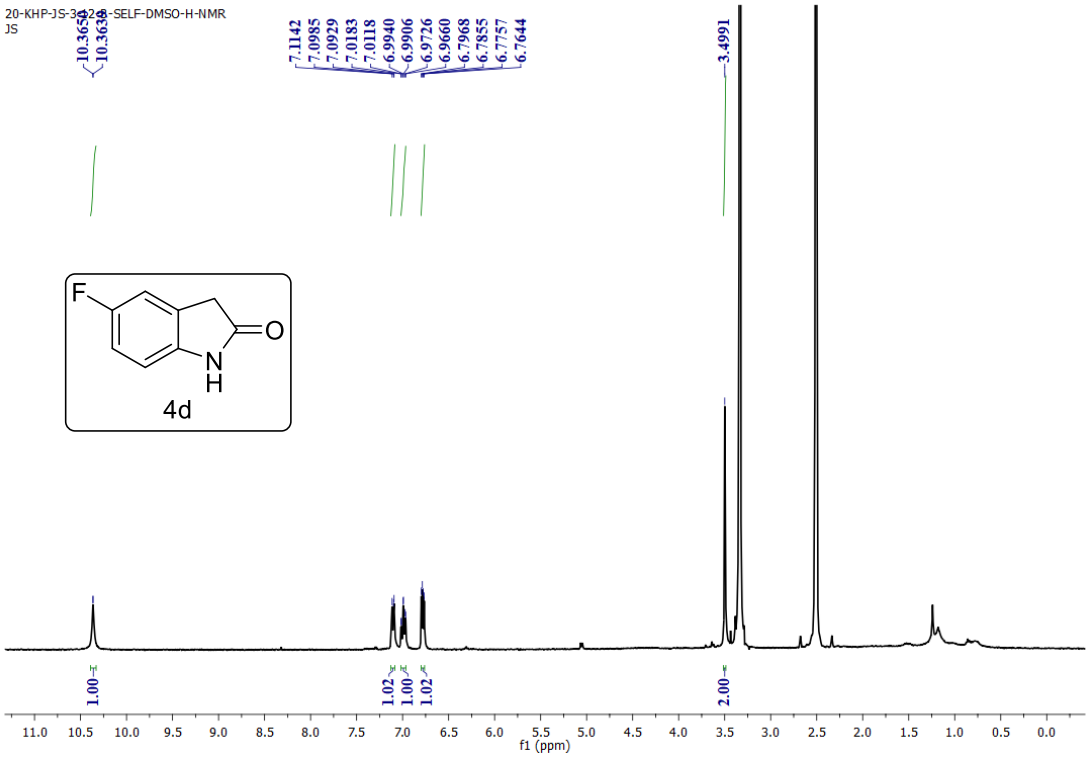
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of 5,7-dimethylindolin-2-one (4c)



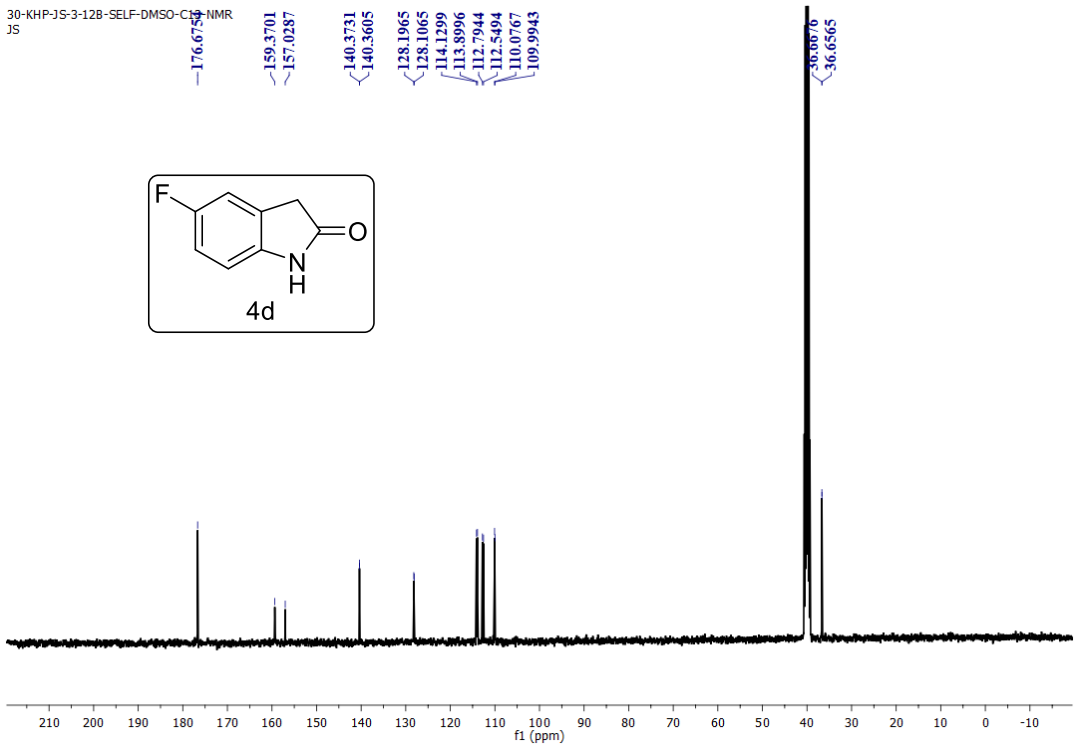
HRMS of 5,7-dimethylindolin-2-one (4c)



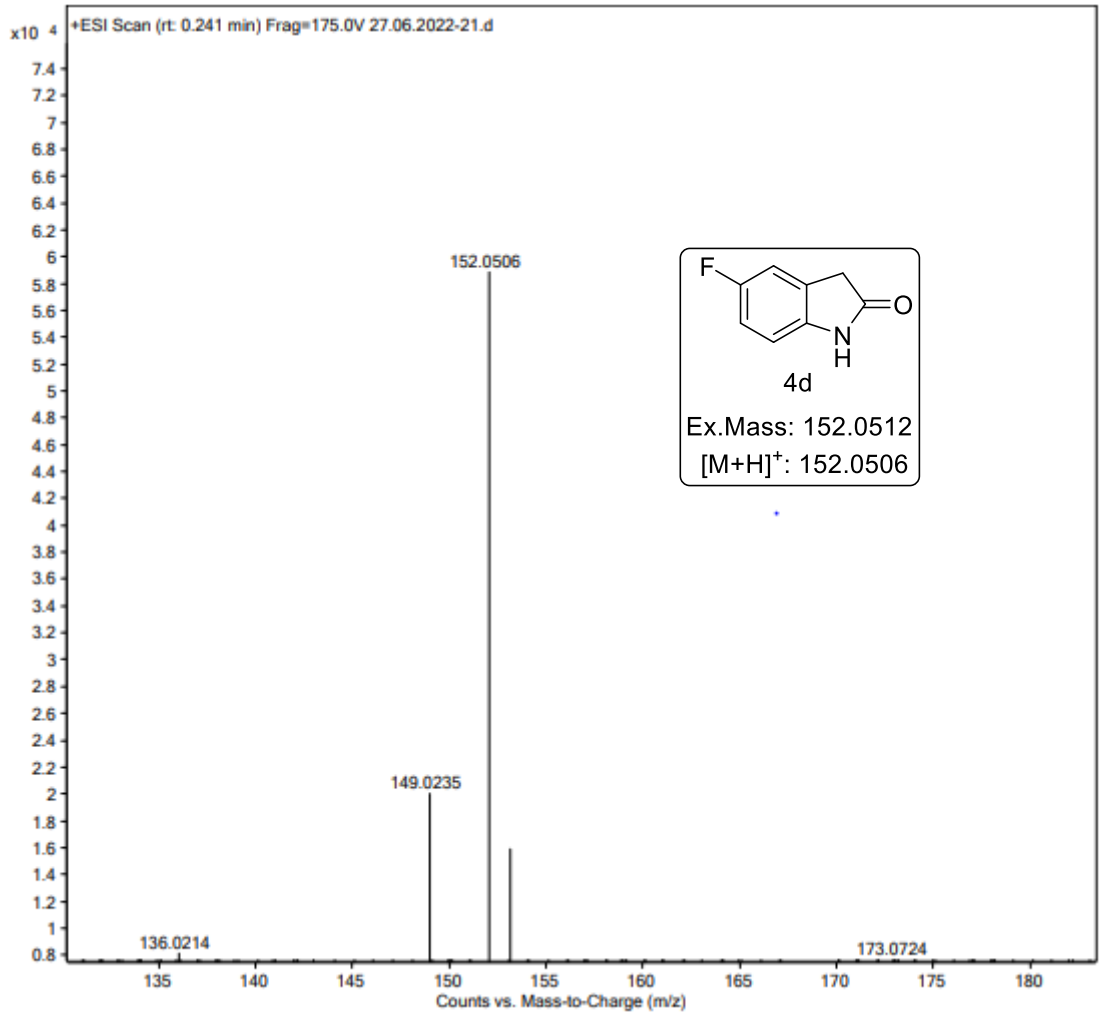
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 5-fluoroindolin-2-one (4d)



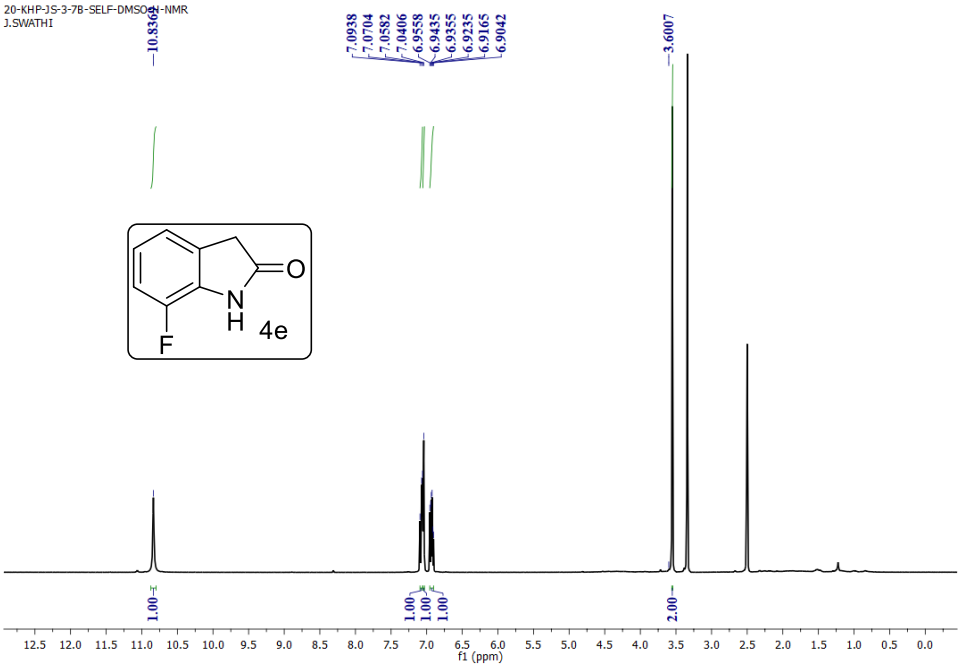
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of 5-fluoroindolin-2-one (4d)



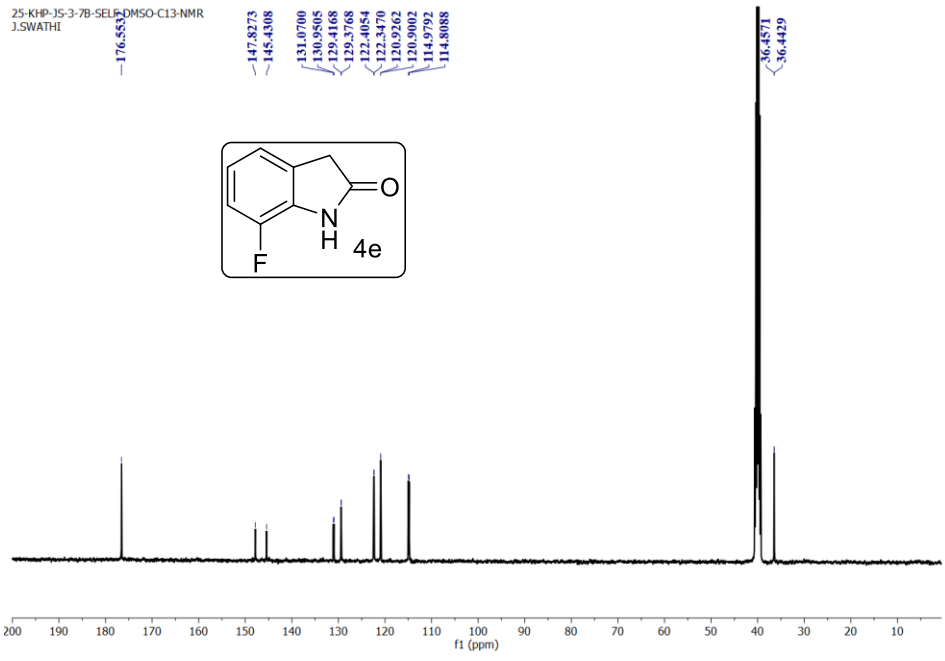
HRMS of 5-fluoroindolin-2-one (4e)



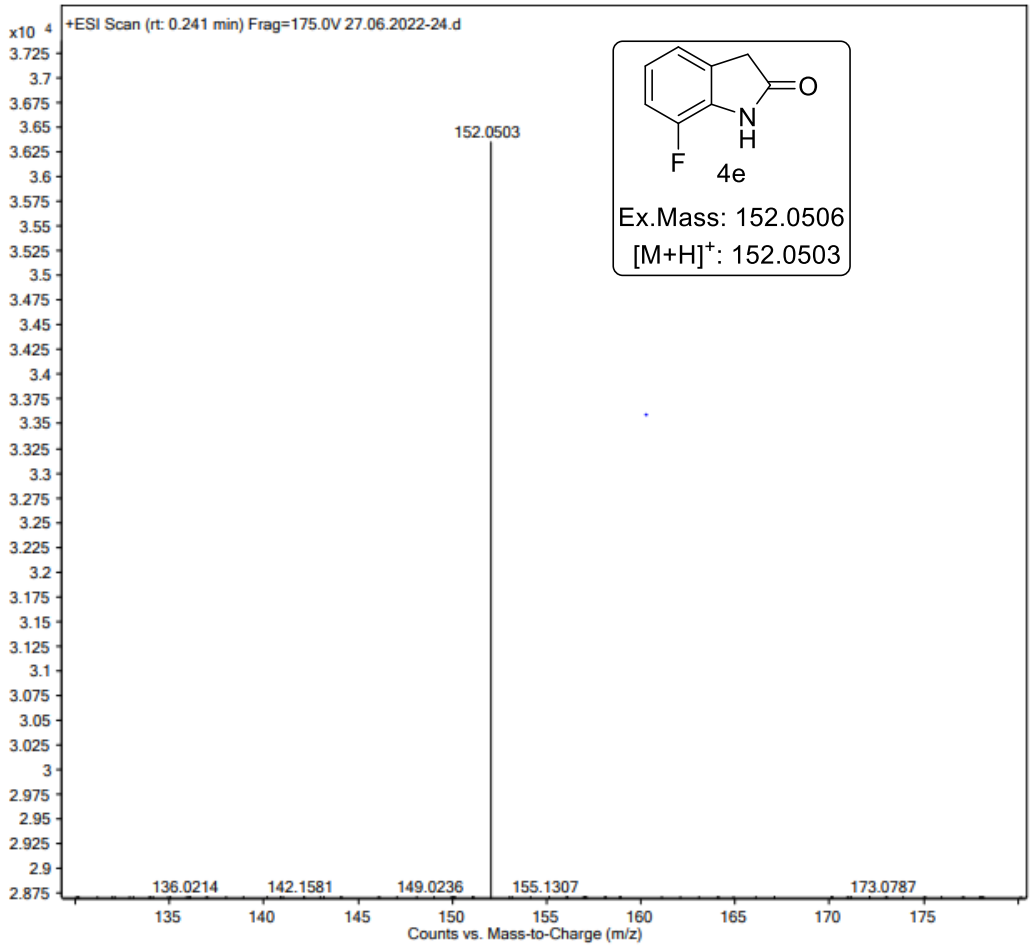
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 7-fluoroindolin-2-one (4e)



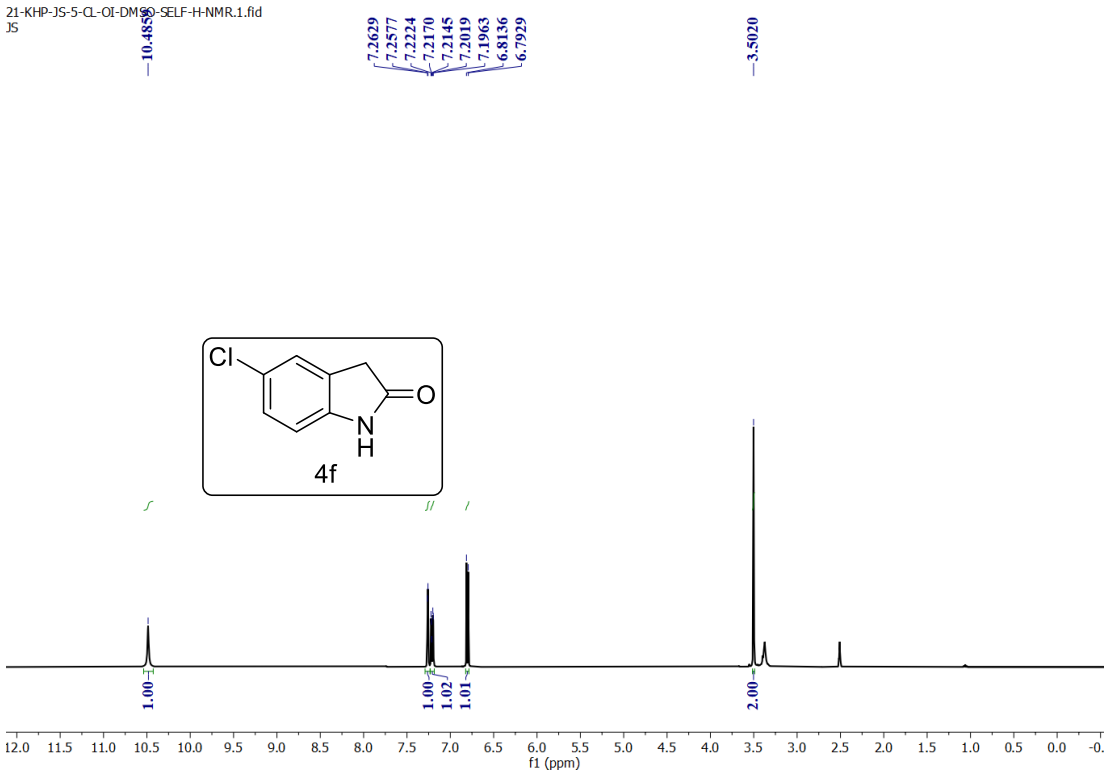
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of 7-fluoroindolin-2-one (4e)



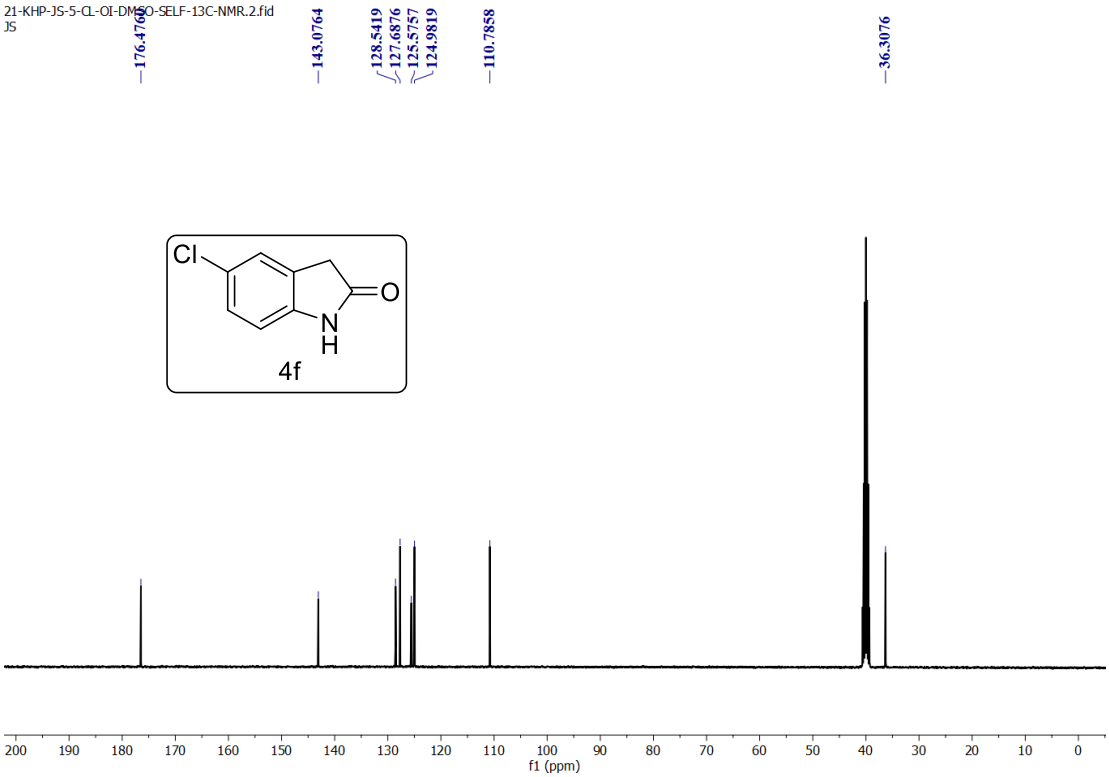
HRMS of 7-fluoroindolin-2-one (4e)



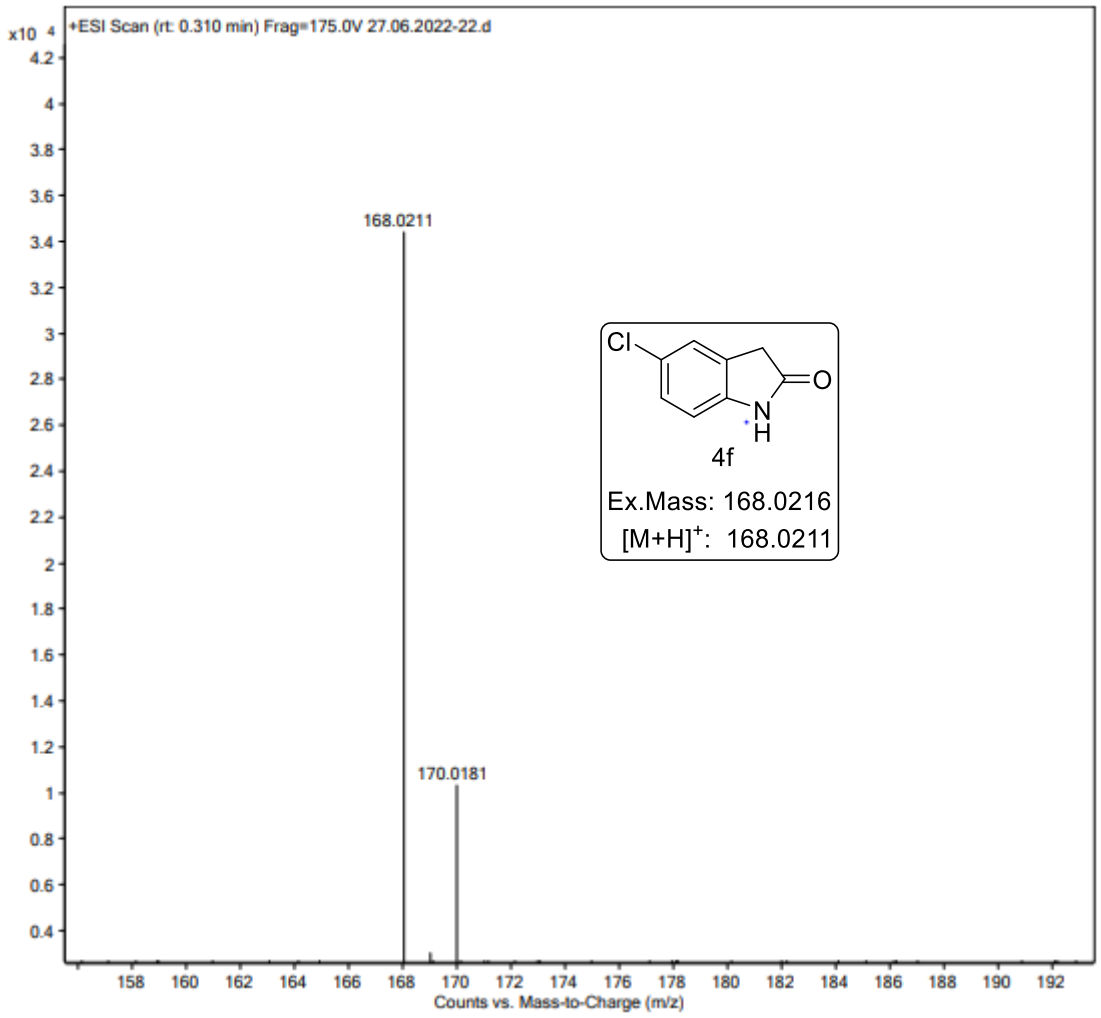
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 5-chloroindolin-2-one (4f)



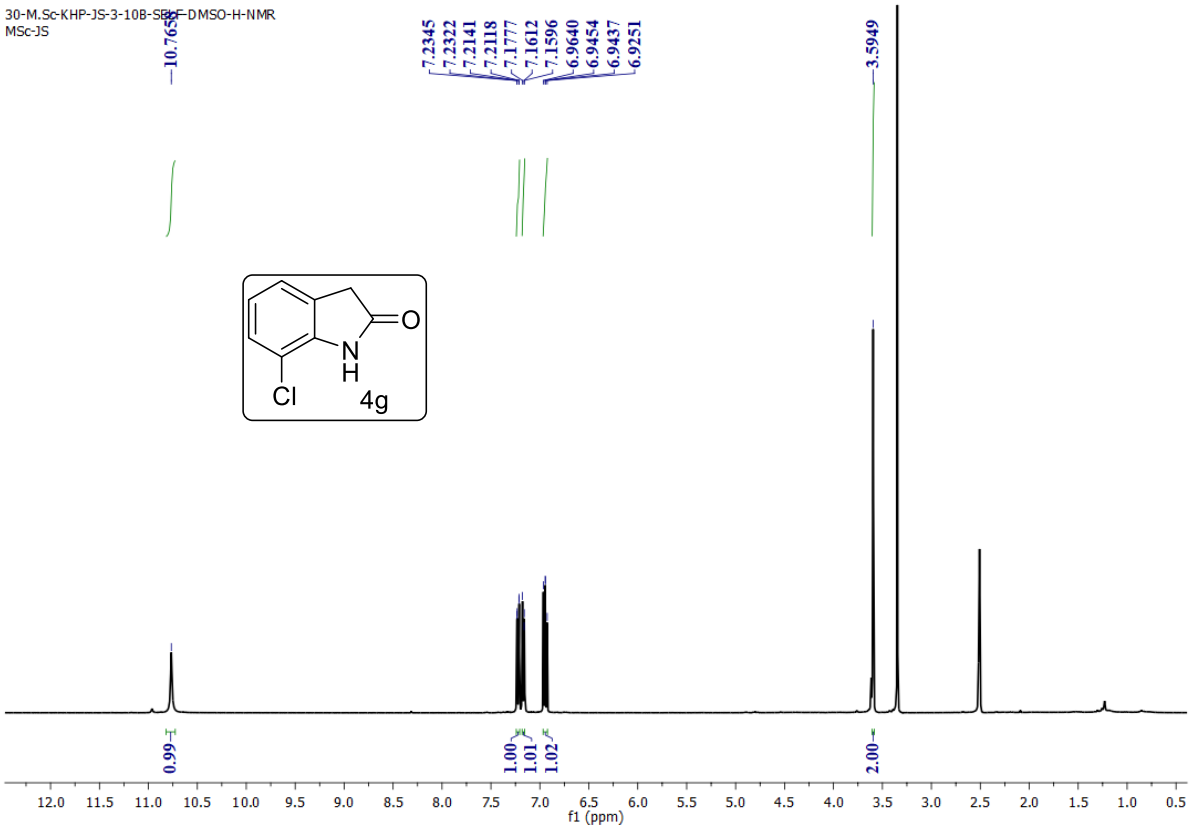
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of 5-chloroindolin-2-one (4f)



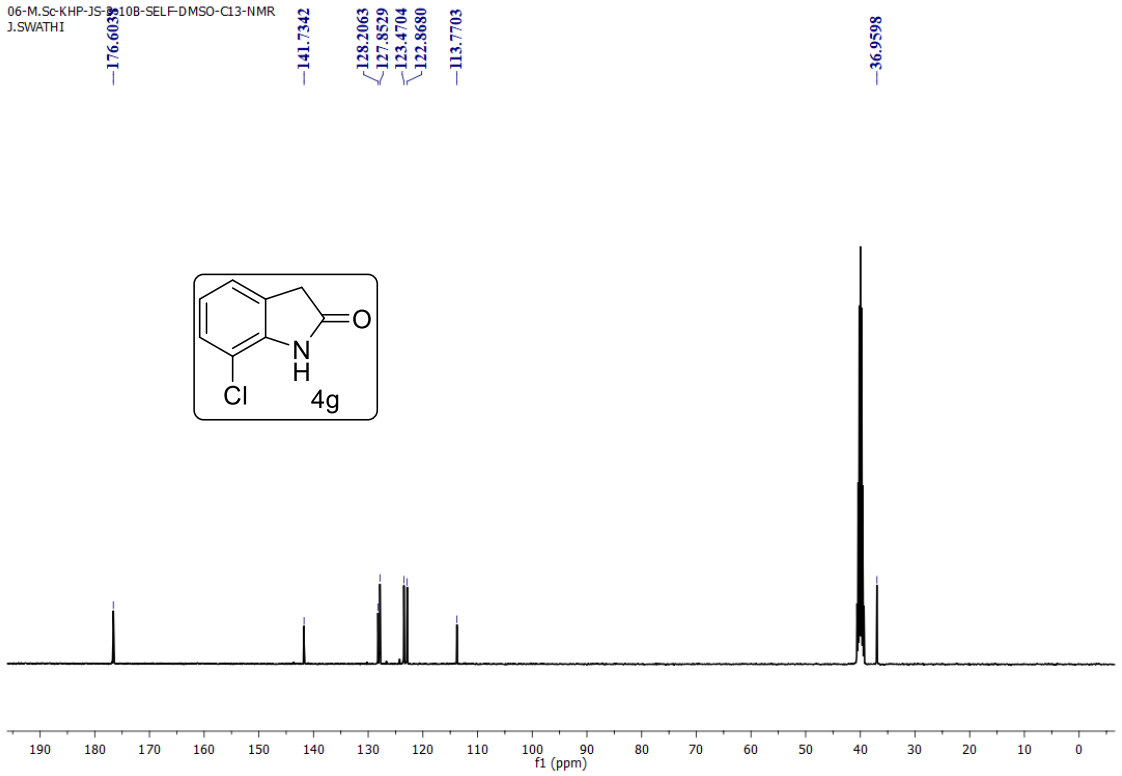
HRMS of 5-chloroindolin-2-one (4f)



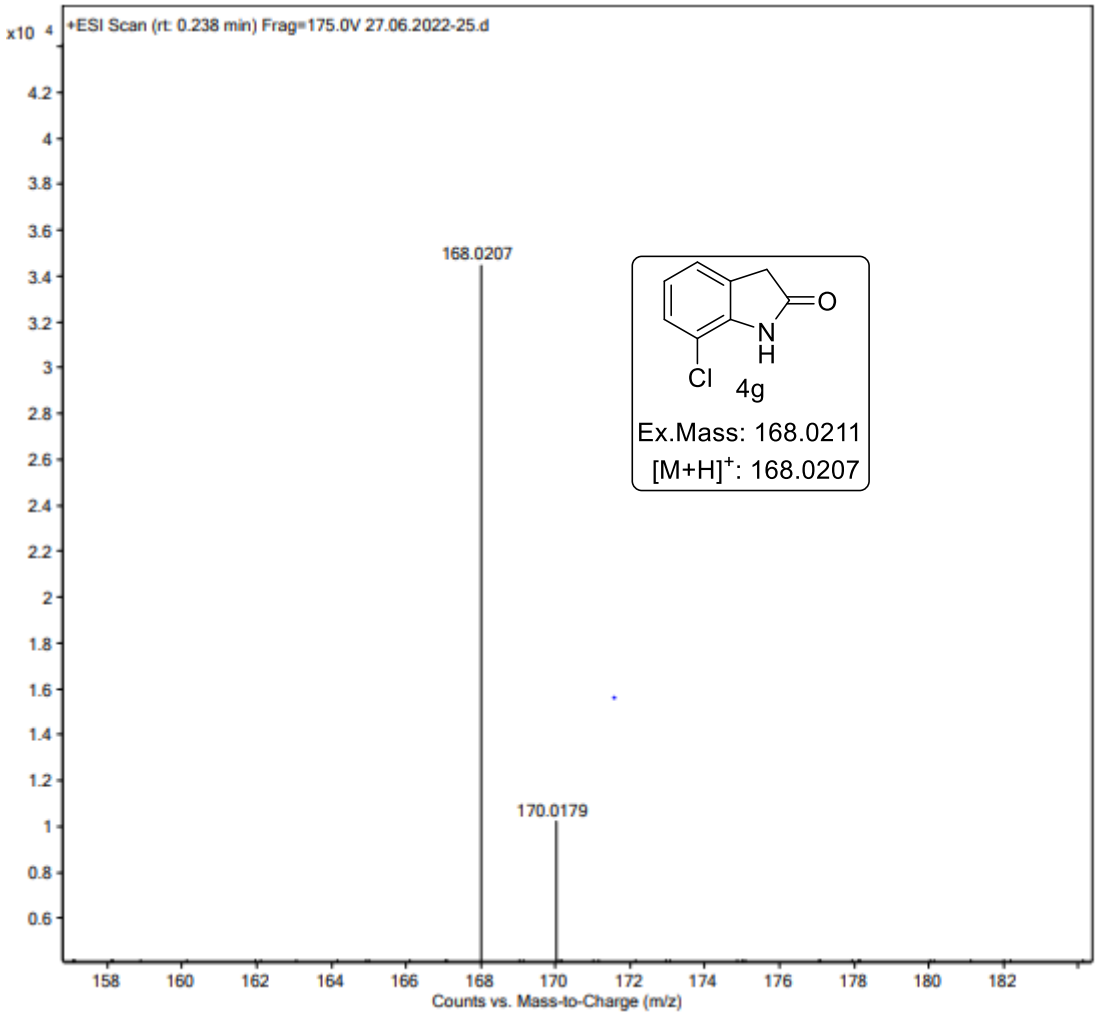
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 7-chloroindolin-2-one (4g)



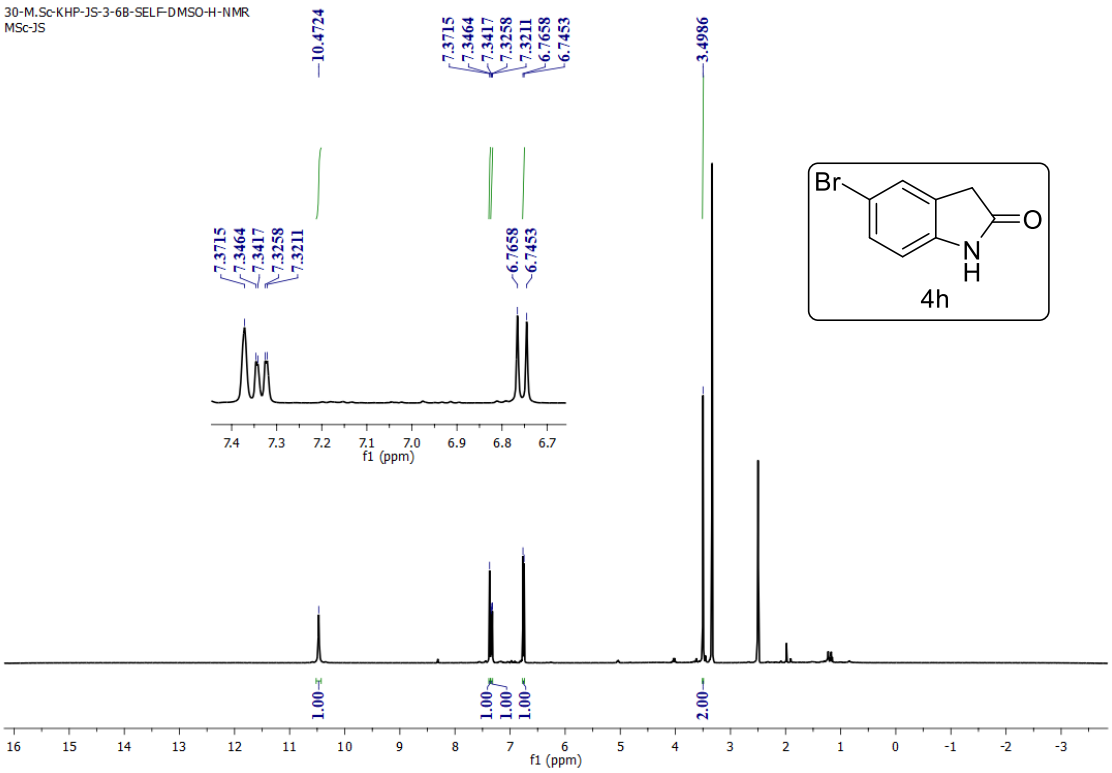
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of 7-chloroindolin-2-one (4g)



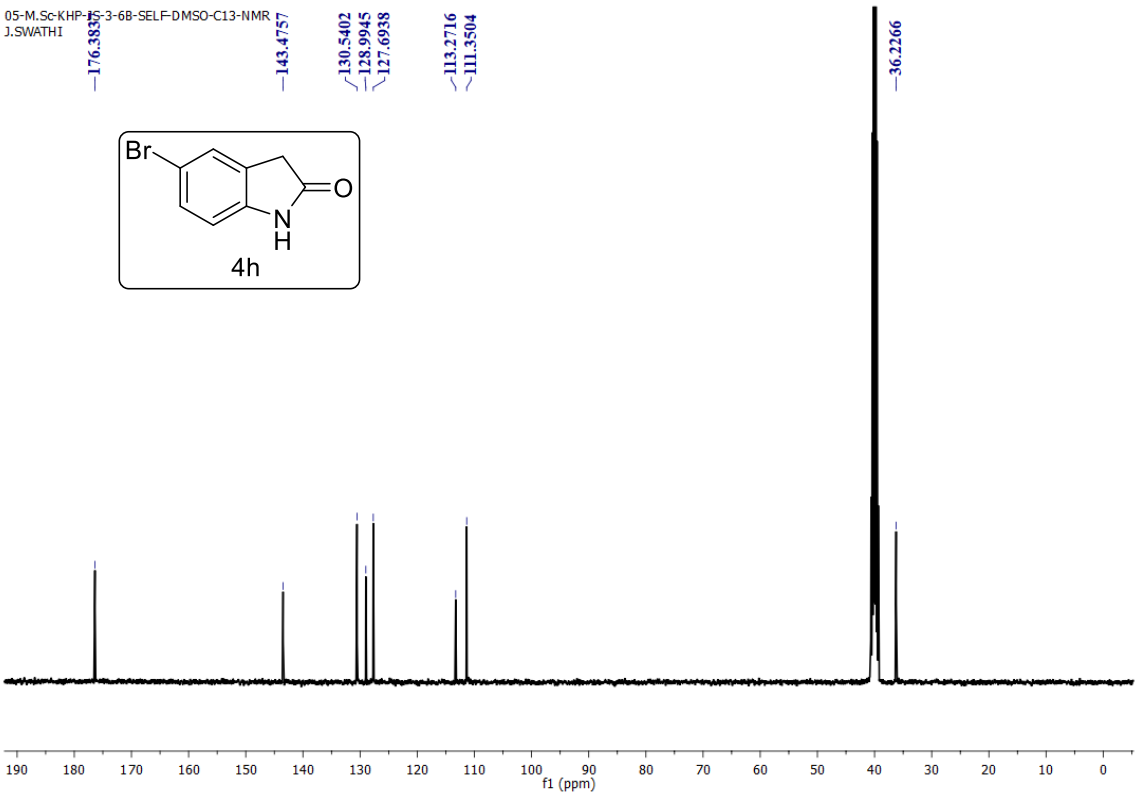
HRMS of 7-chloroindolin-2-one (4j)



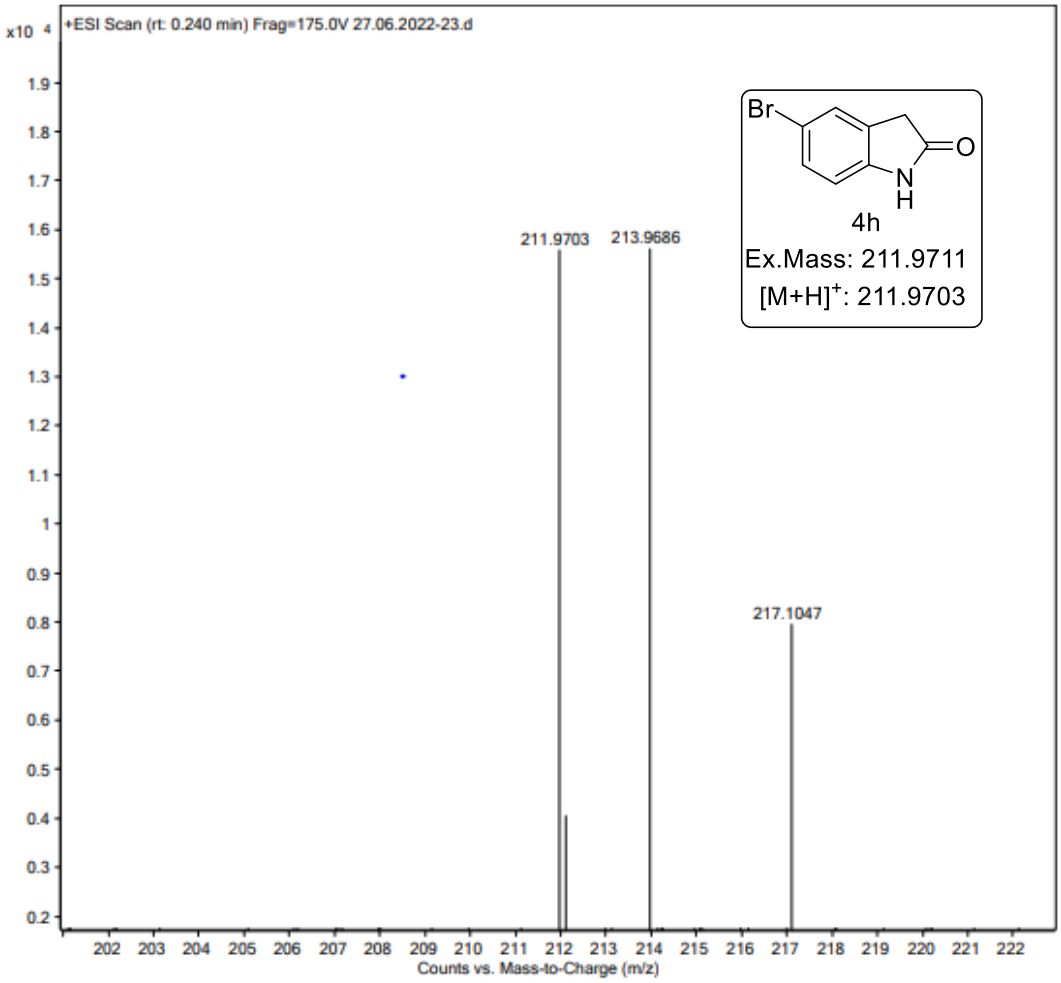
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 5-bromoindolin-2-one (4h)



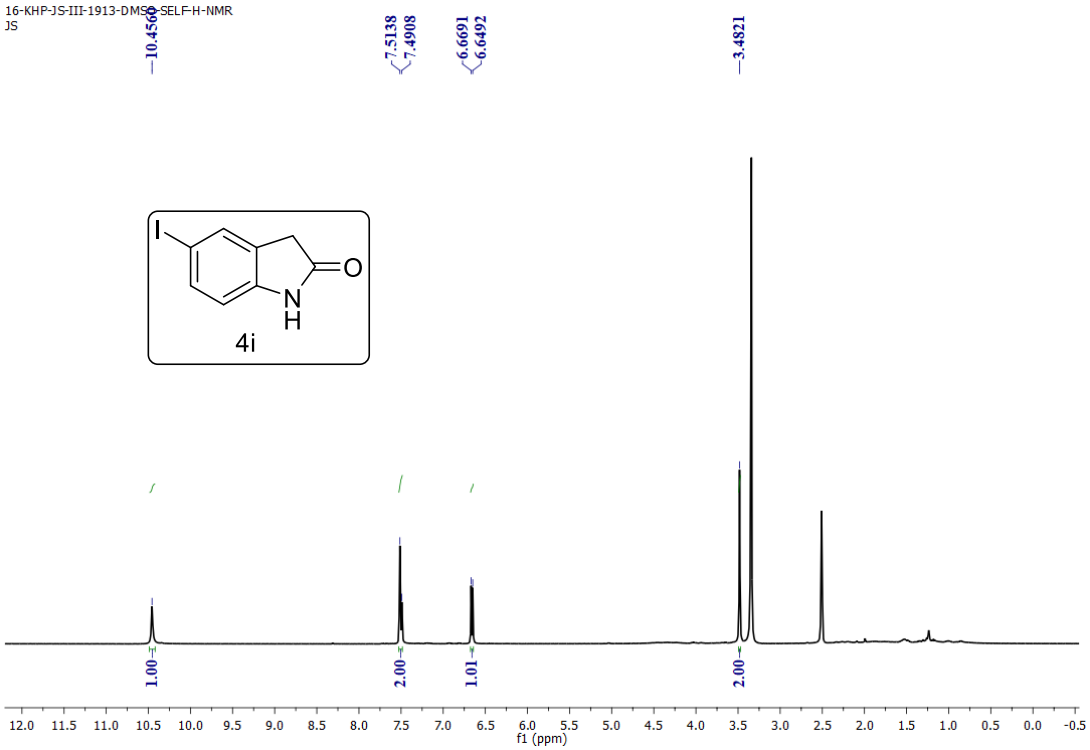
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of 5-bromoindolin-2-one (4h)



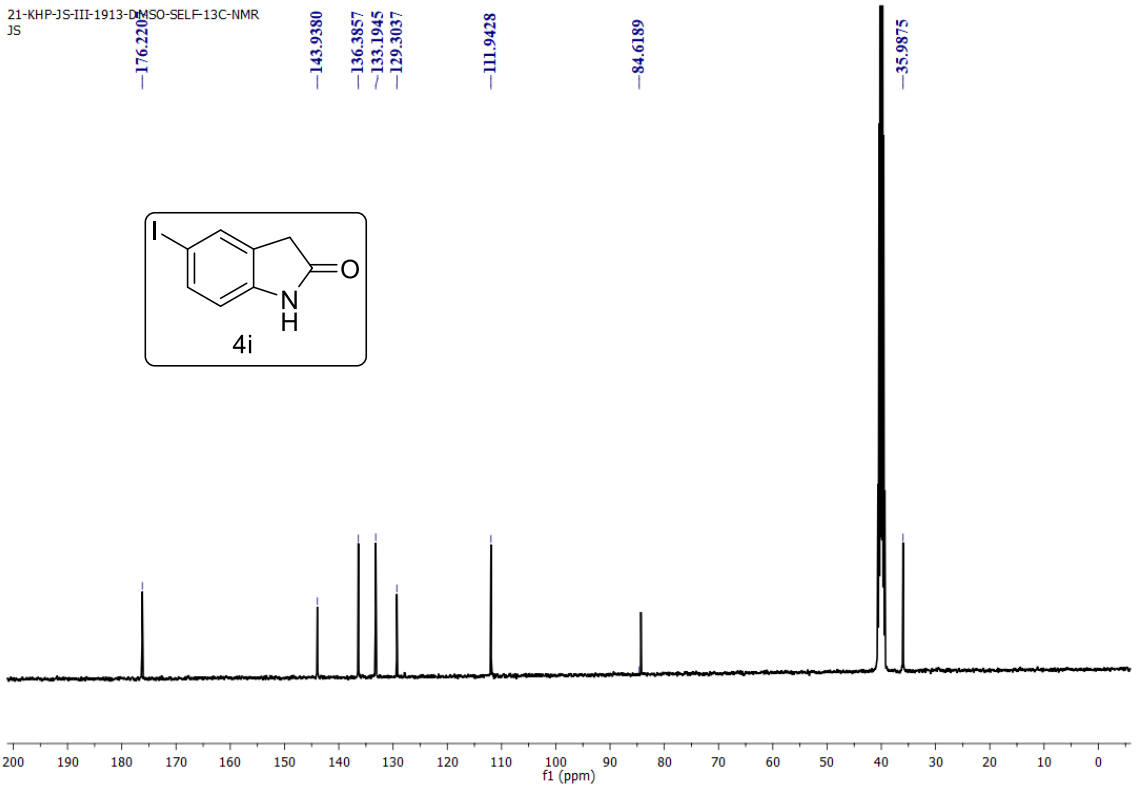
HRMS of 5-bromoindolin-2-one (4g)



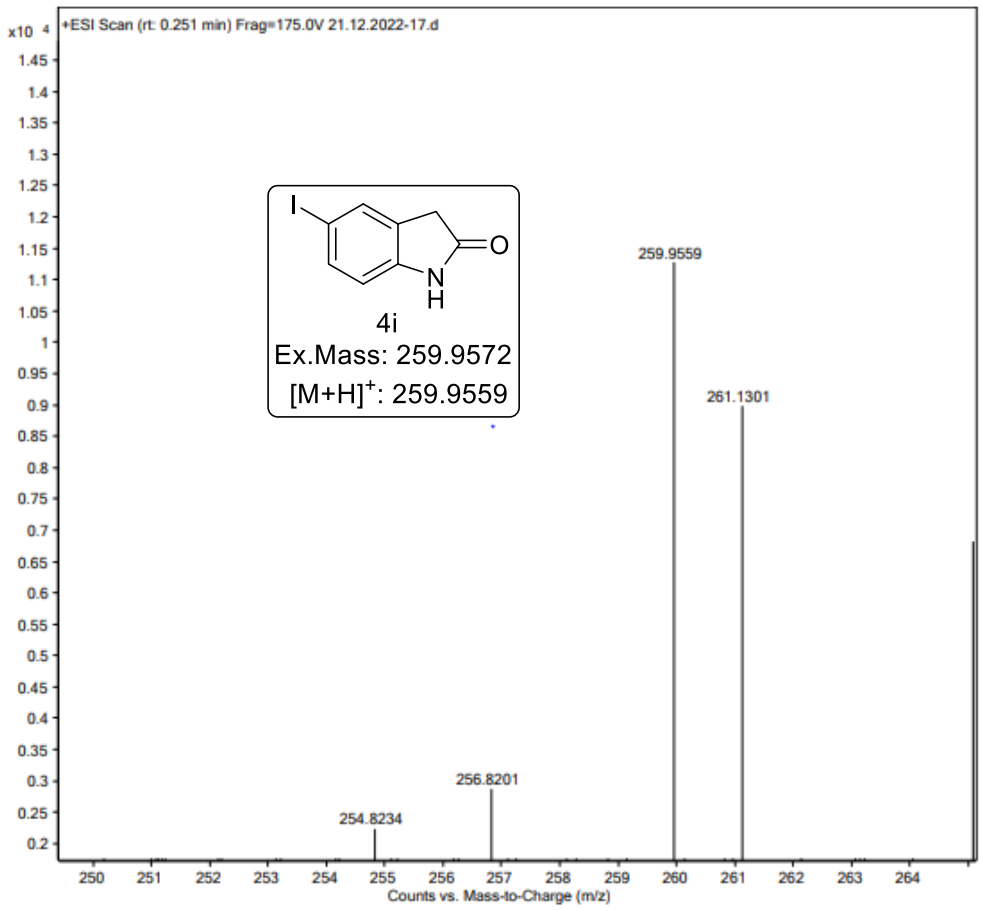
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 5-iodoindolin-2-one (4i)



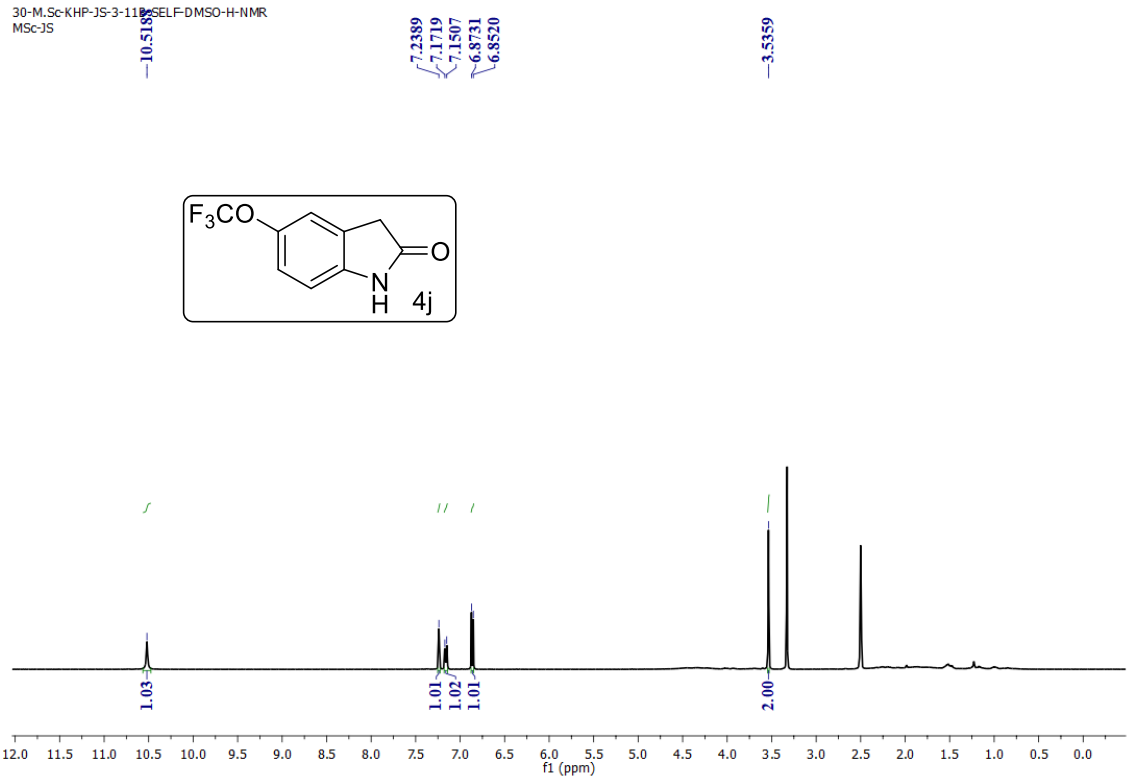
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of 5-iodoindolin-2-one (4i)



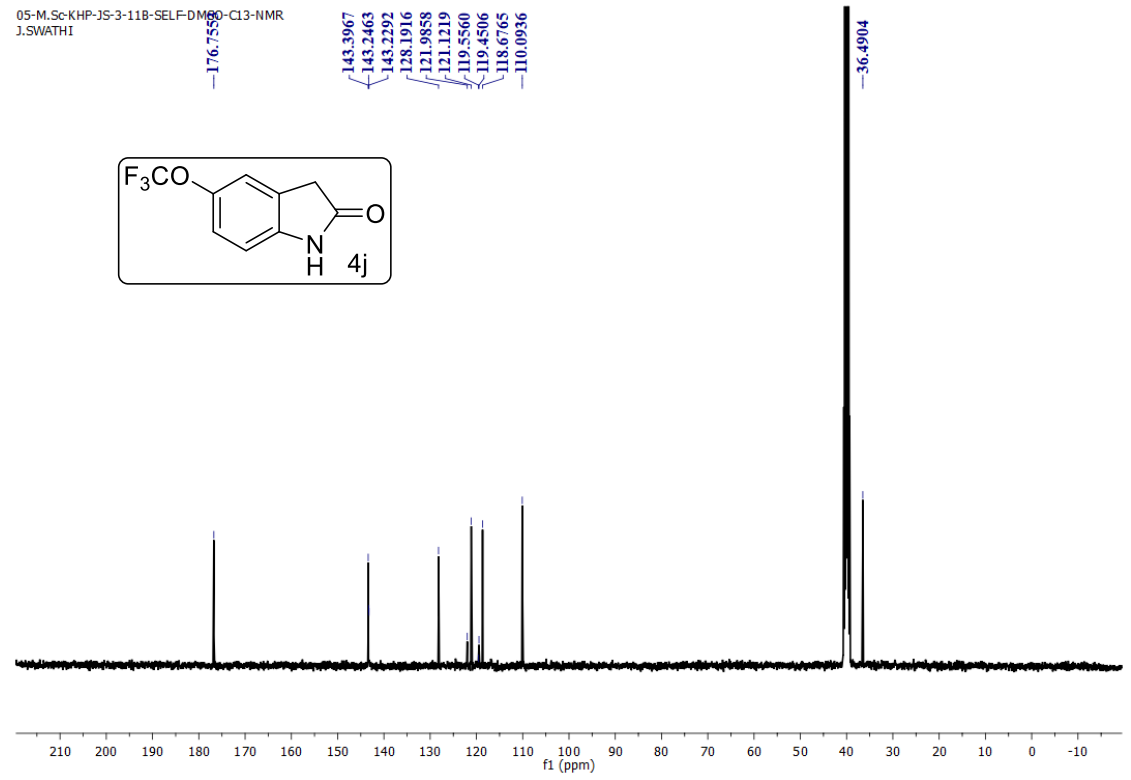
HRMS of 5-iodoindolin-2-one (4i)



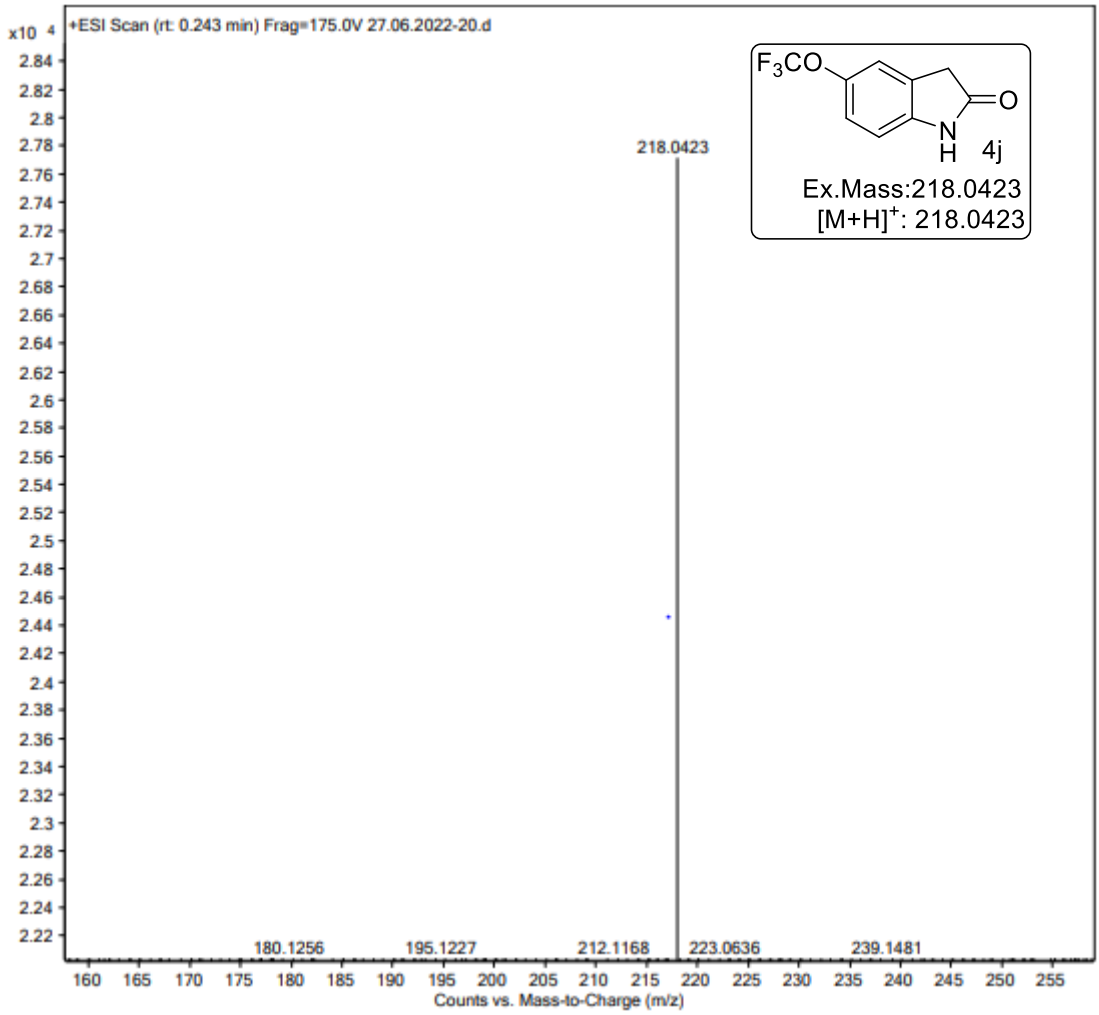
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 5-(trifluoromethoxy)indolin-2-one (4j)



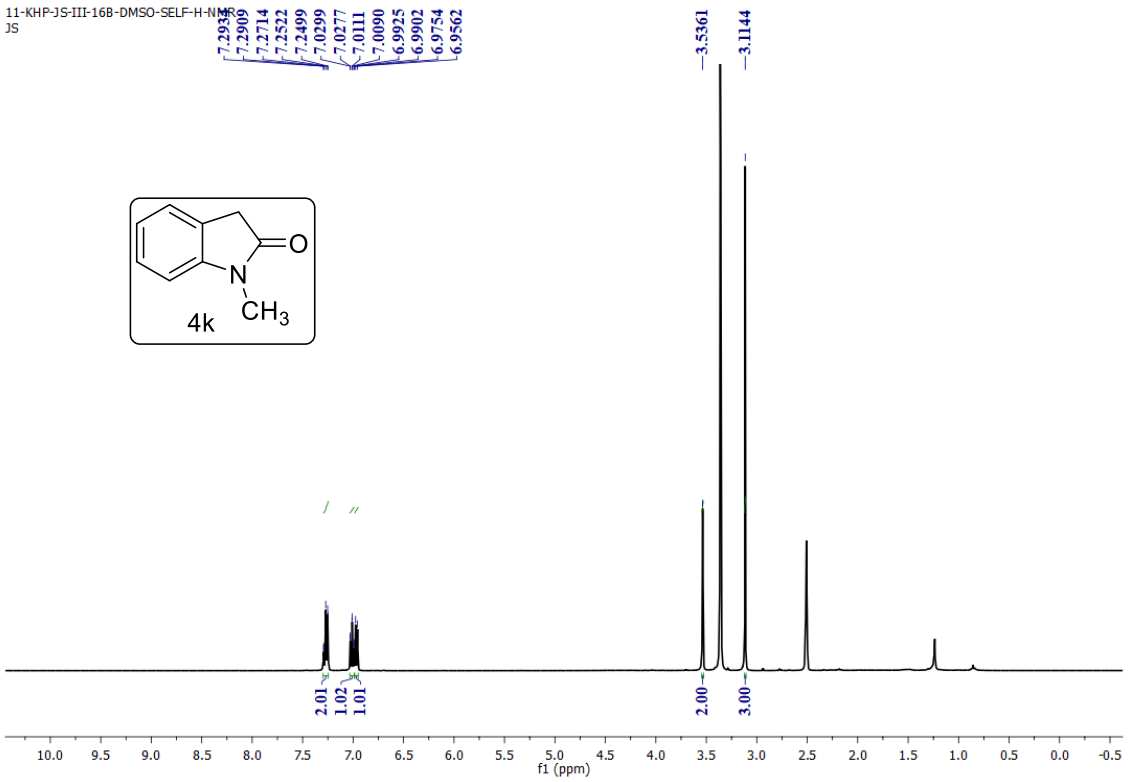
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of 5-(trifluoromethoxy)indolin-2-one (4j)



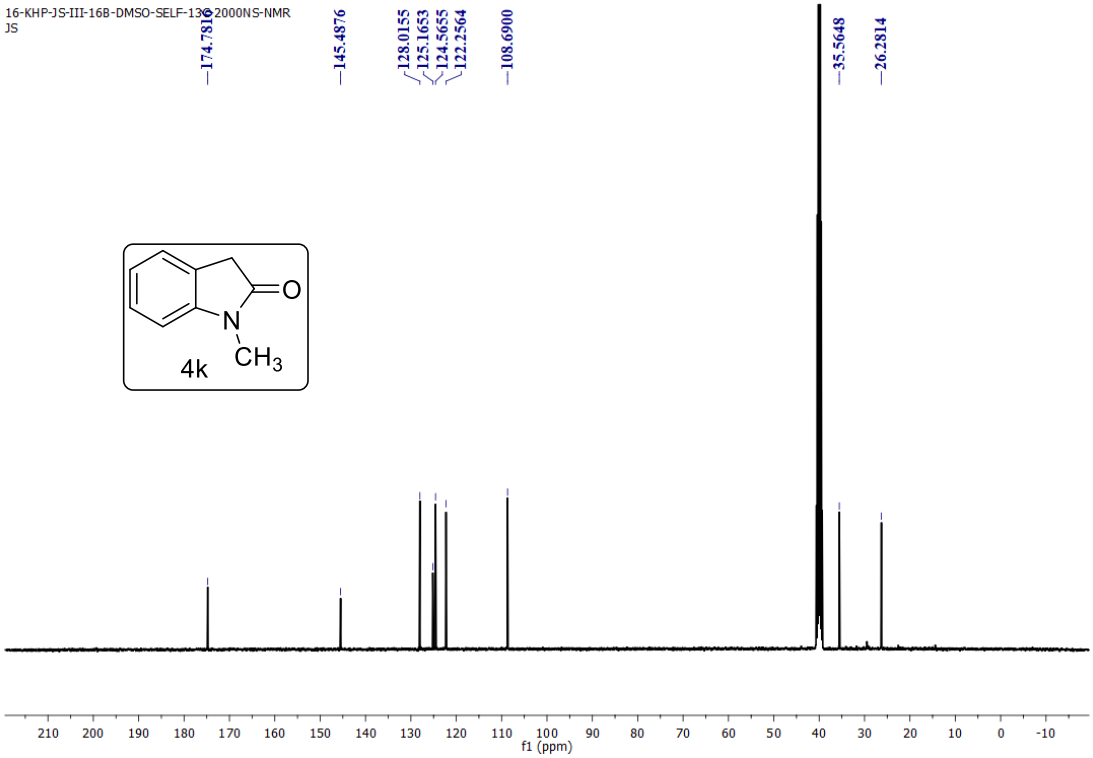
HRMS of 5-(trifluoromethoxy)indolin-2-one (4j)



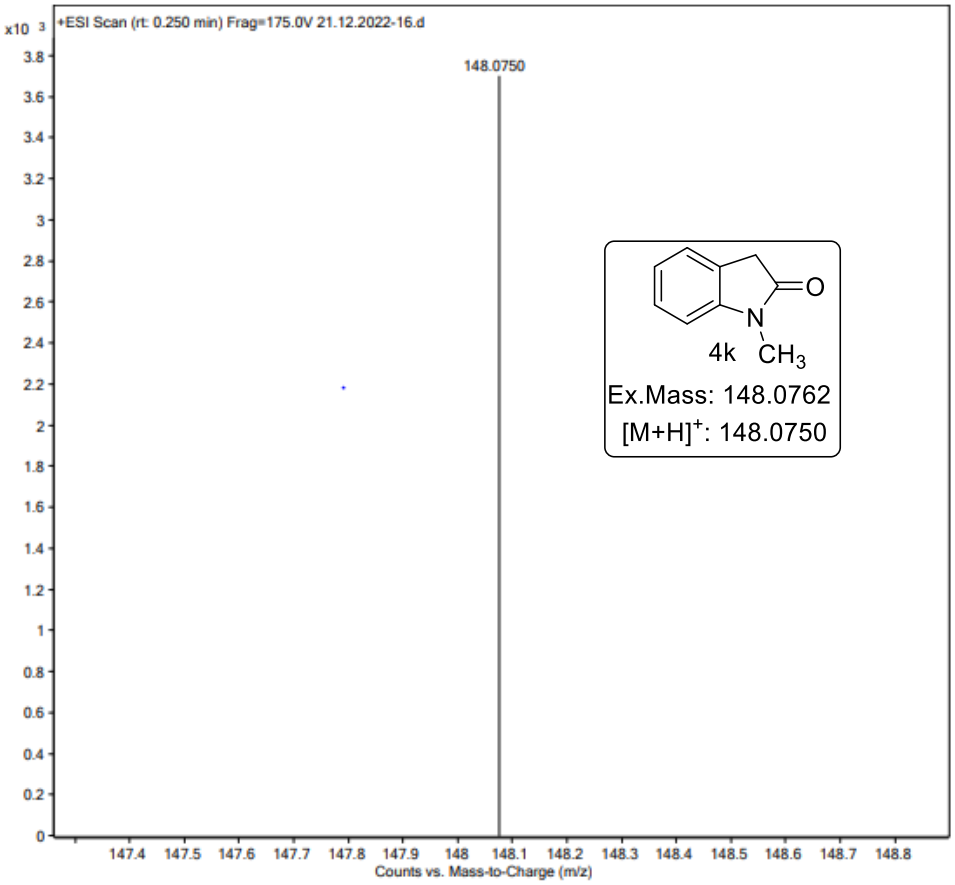
^{1}H NMR (400 MHz, DMSO-d_6) 1-methylindolin-2-one (4k)



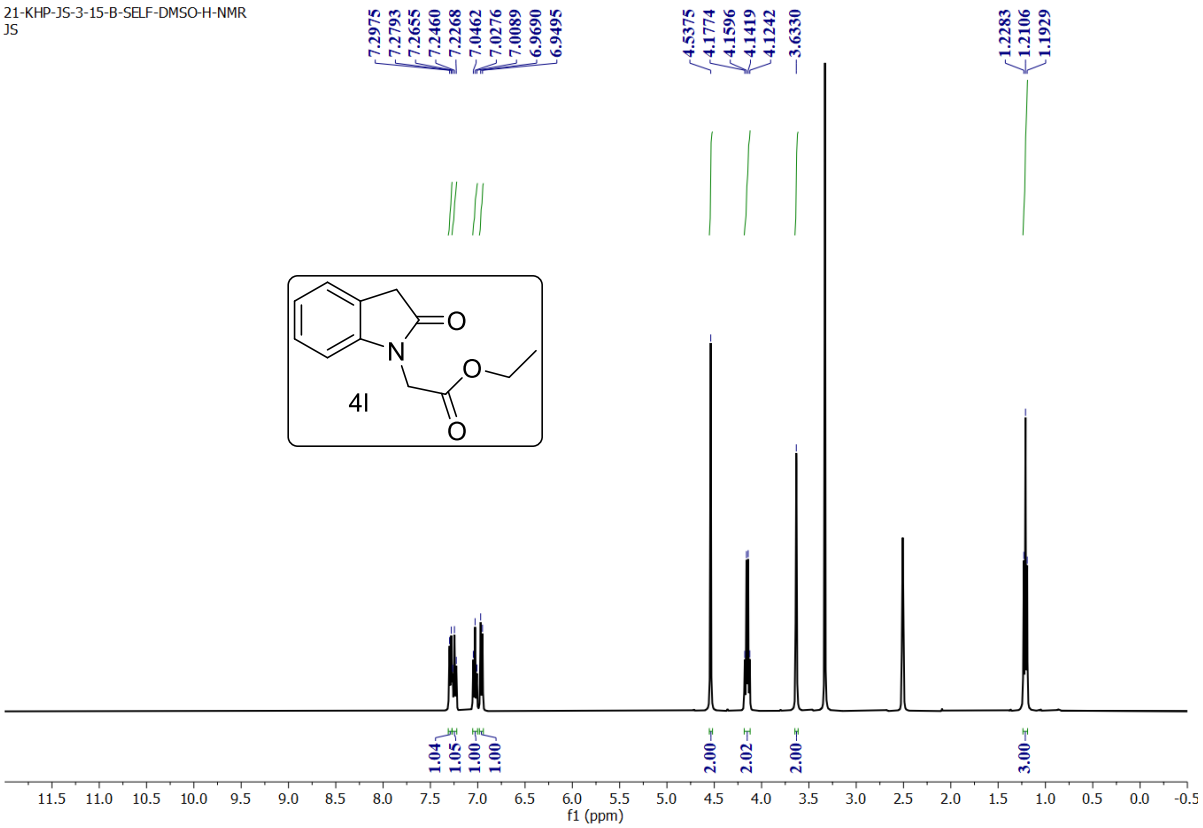
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of 1-methylindolin-2-one (4k)



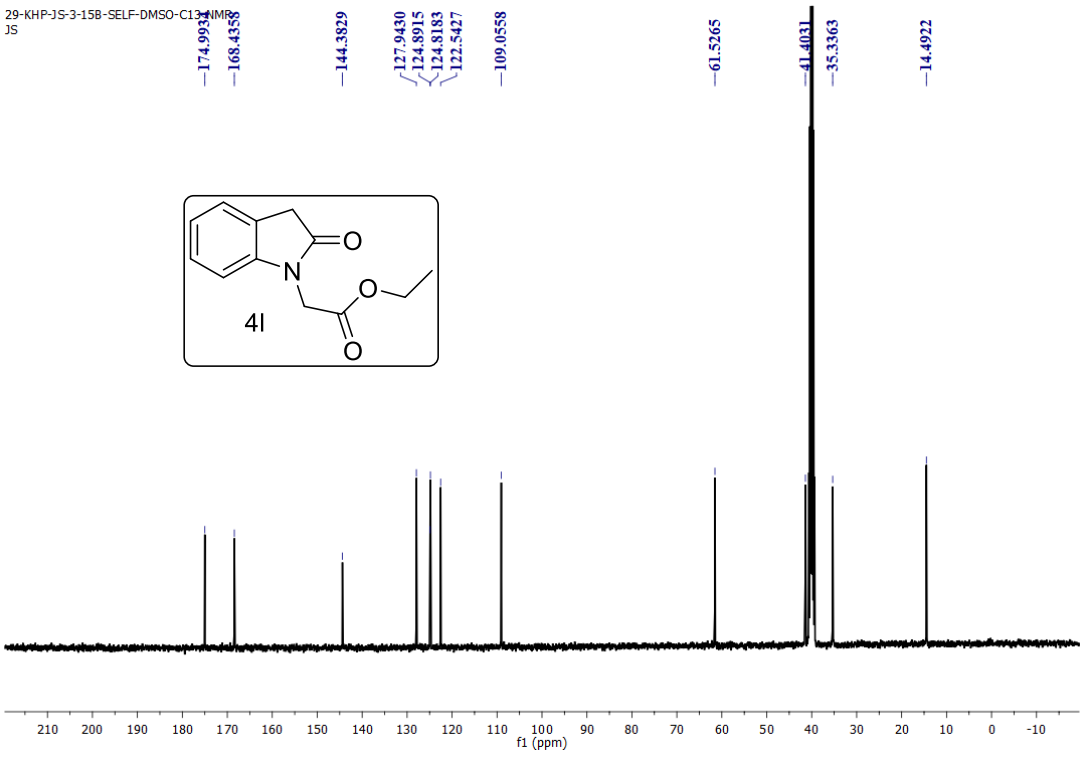
HRMS of 1-methylindolin-2-one (4k)



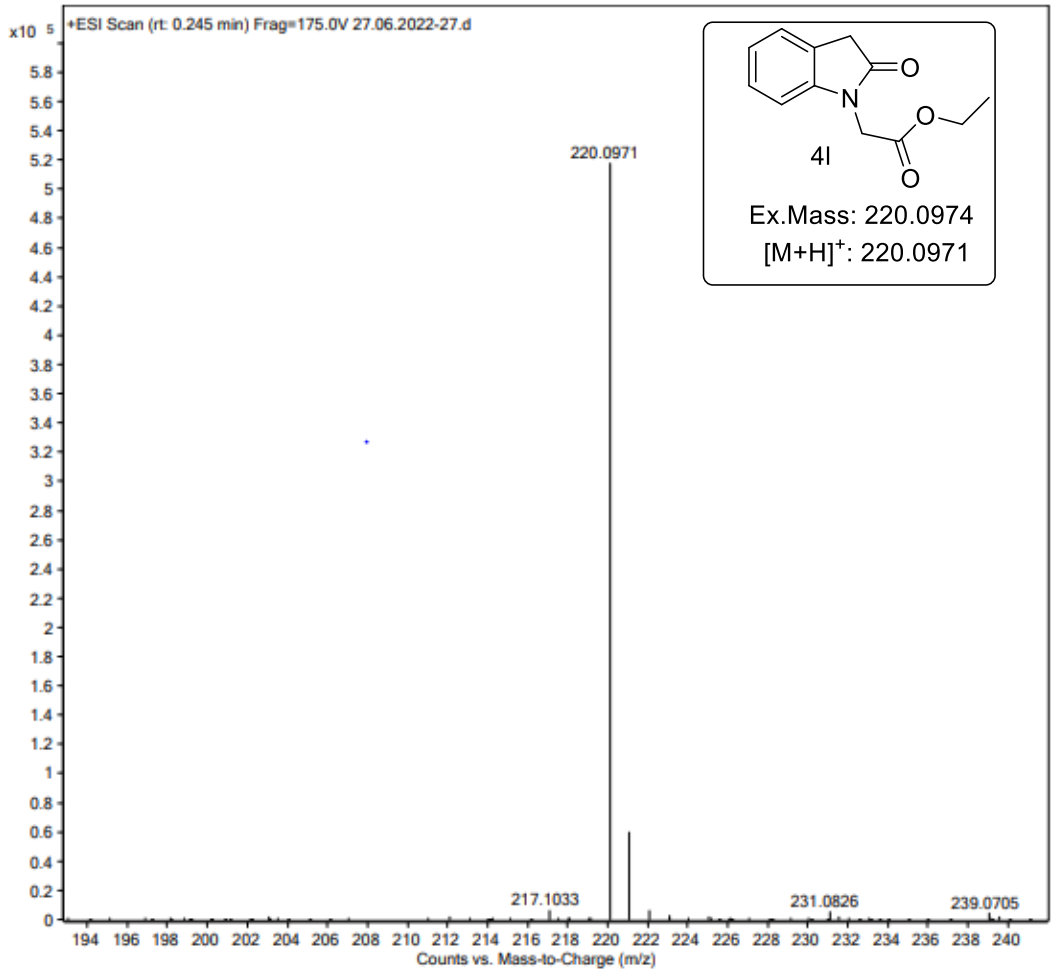
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of ethyl 2-(2-oxoindolin-1-yl)acetate (4l)



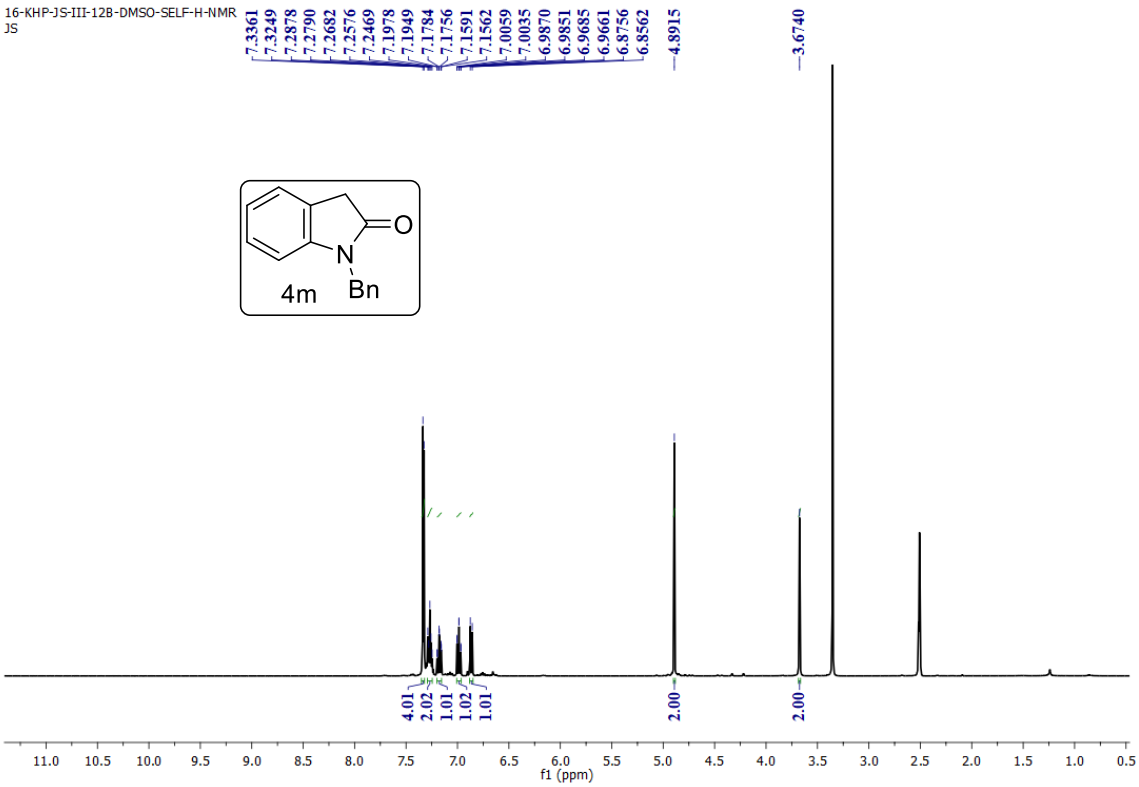
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of ethyl 2-(2-oxoindolin-1-yl)acetate (4l)



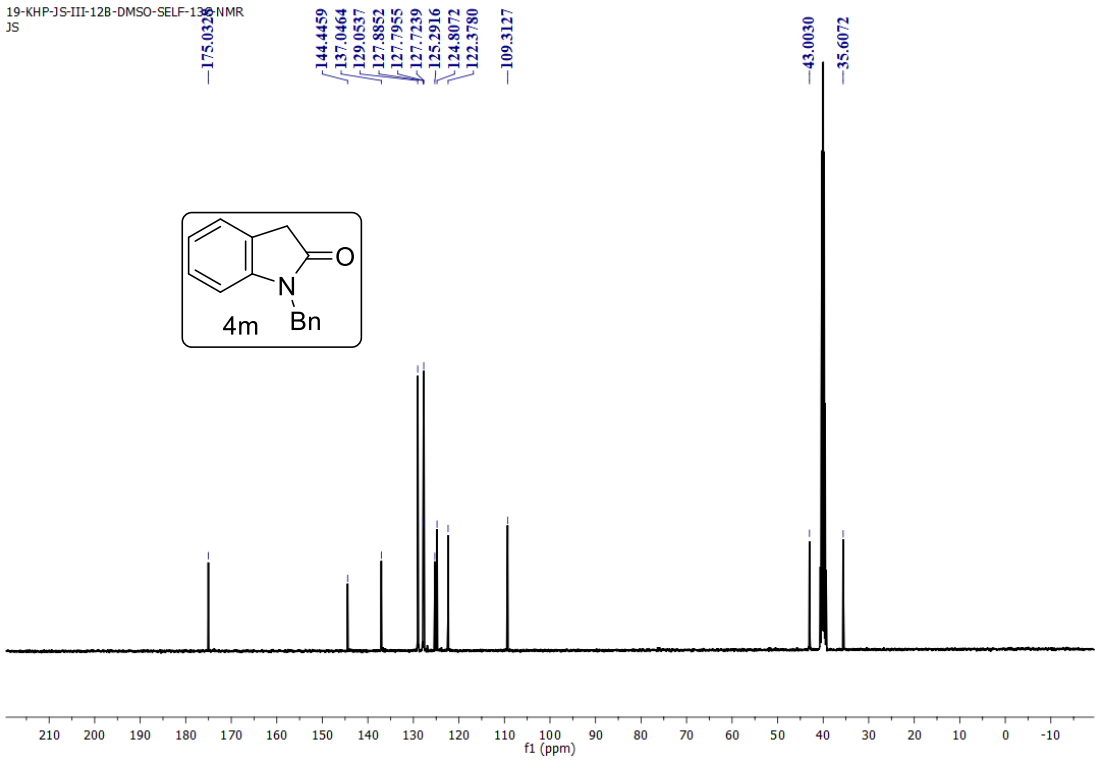
HRMS of ethyl 2-(2-oxoindolin-1-yl)acetate (4l)



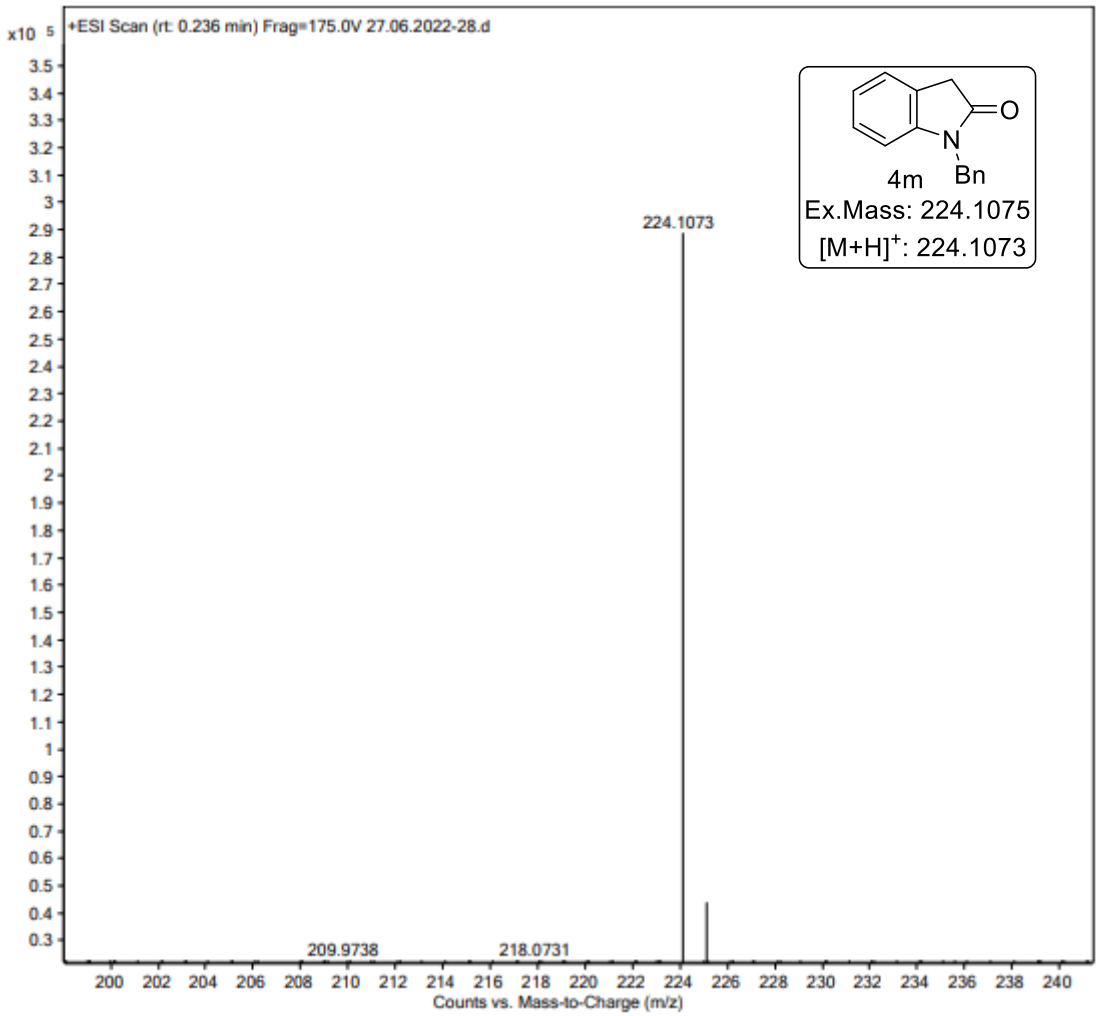
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 1-benzylindolin-2-one (4m)



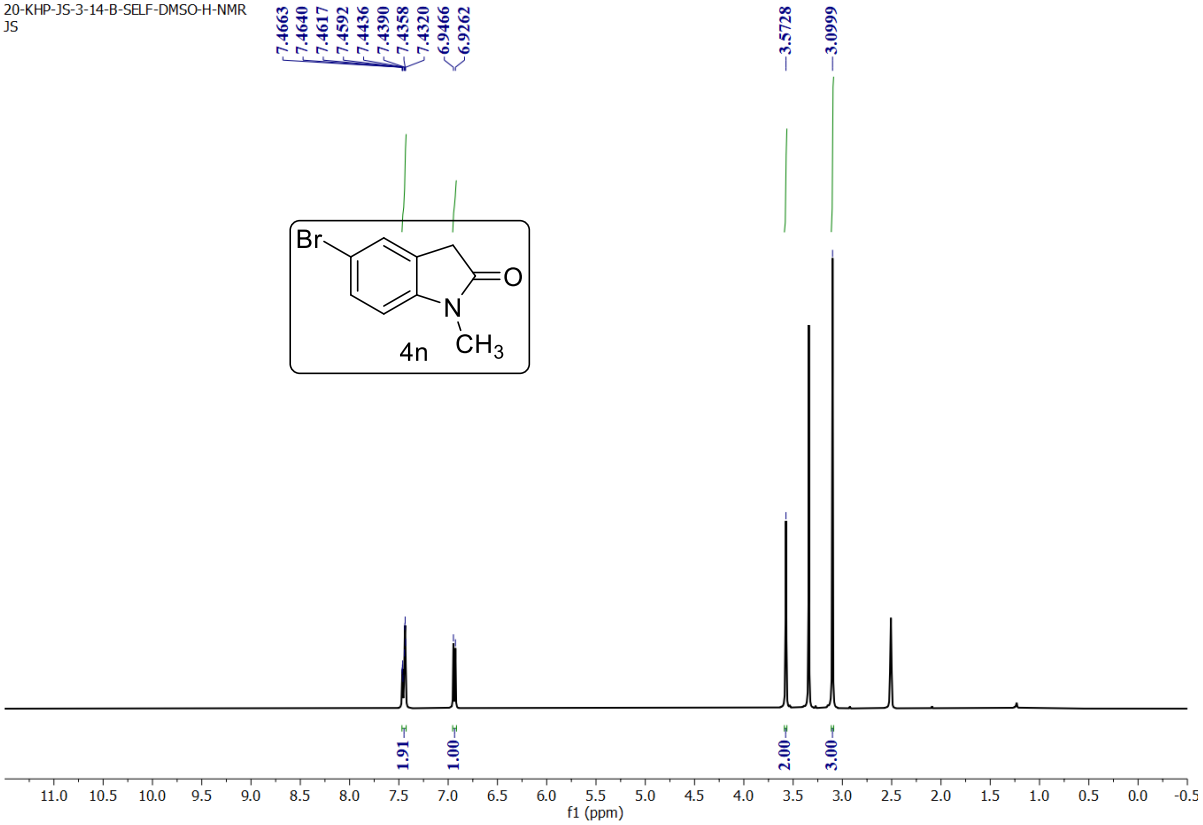
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of 1-benzylindolin-2-one (4m)



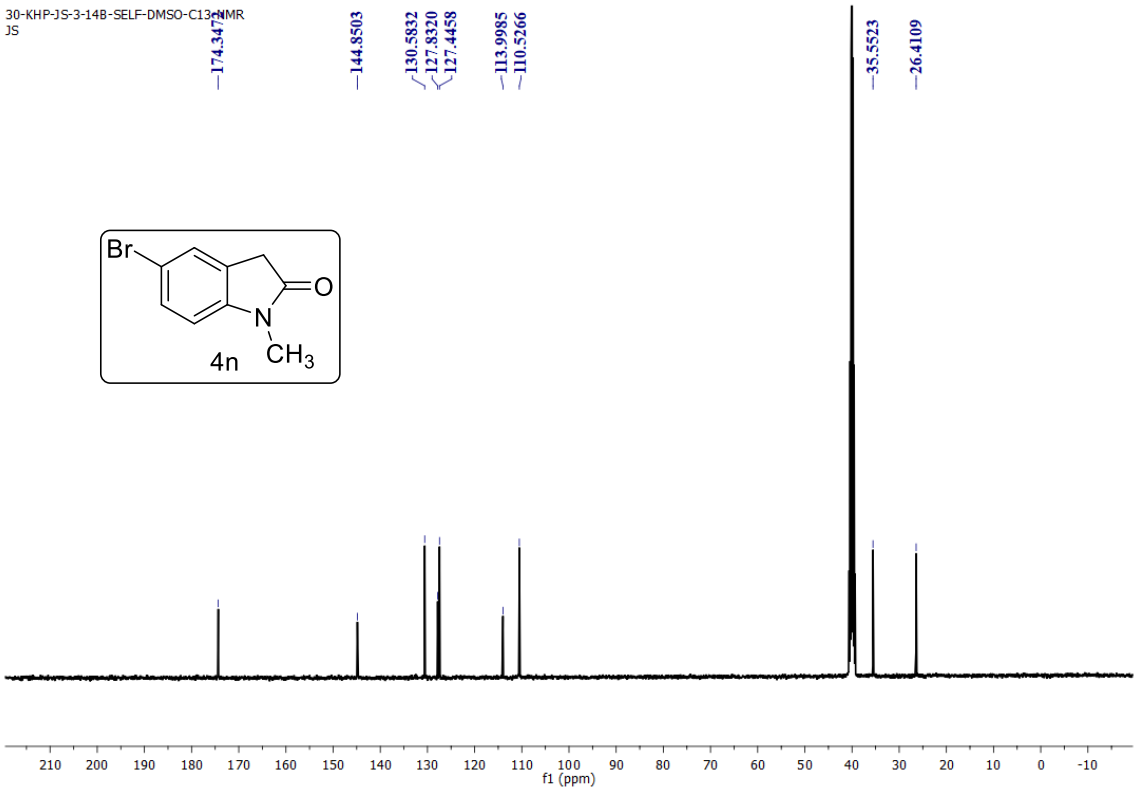
HRMS of 1-benzylindolin-2-one (4m)



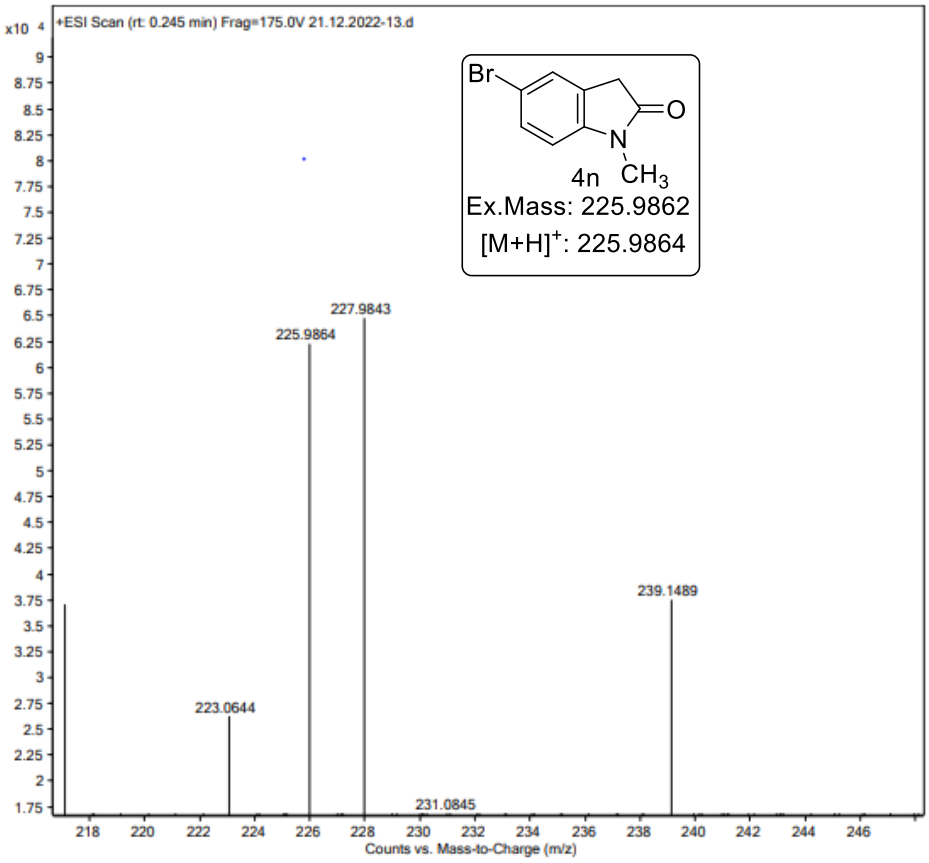
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 5-bromo-1-methylindolin-2-one (4n)



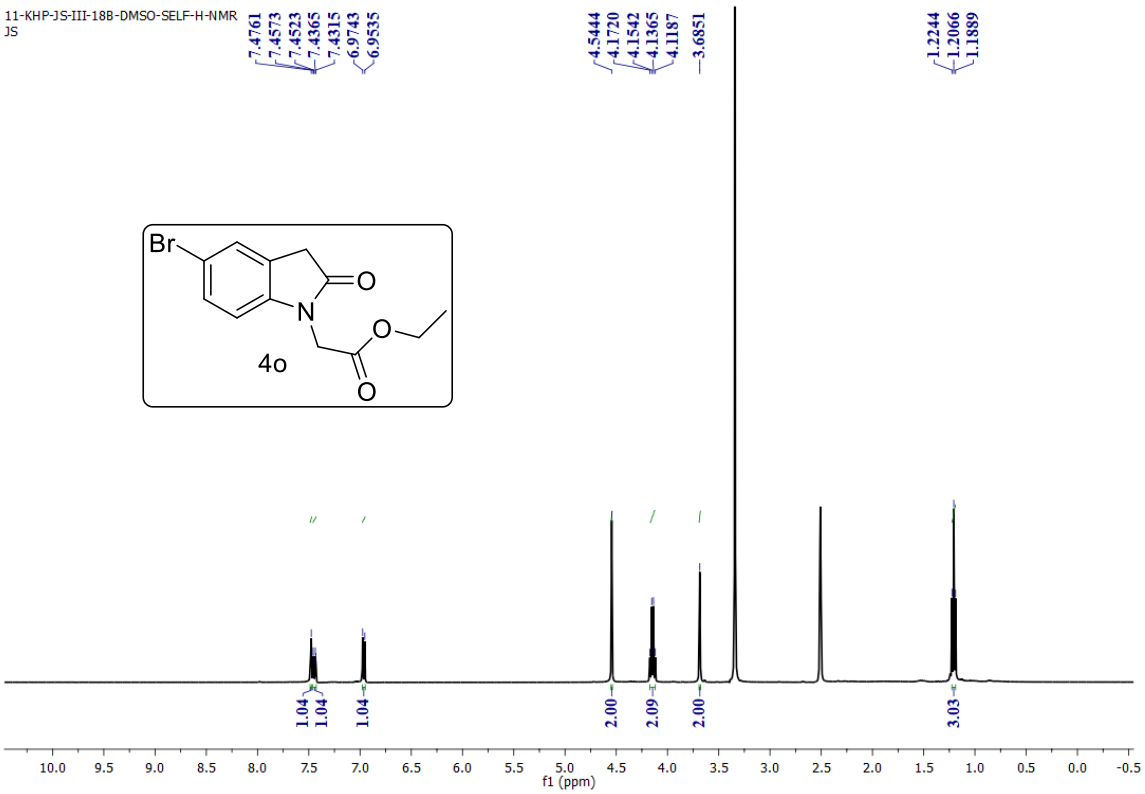
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of 5-bromo-1-methylindolin-2-one (4n)



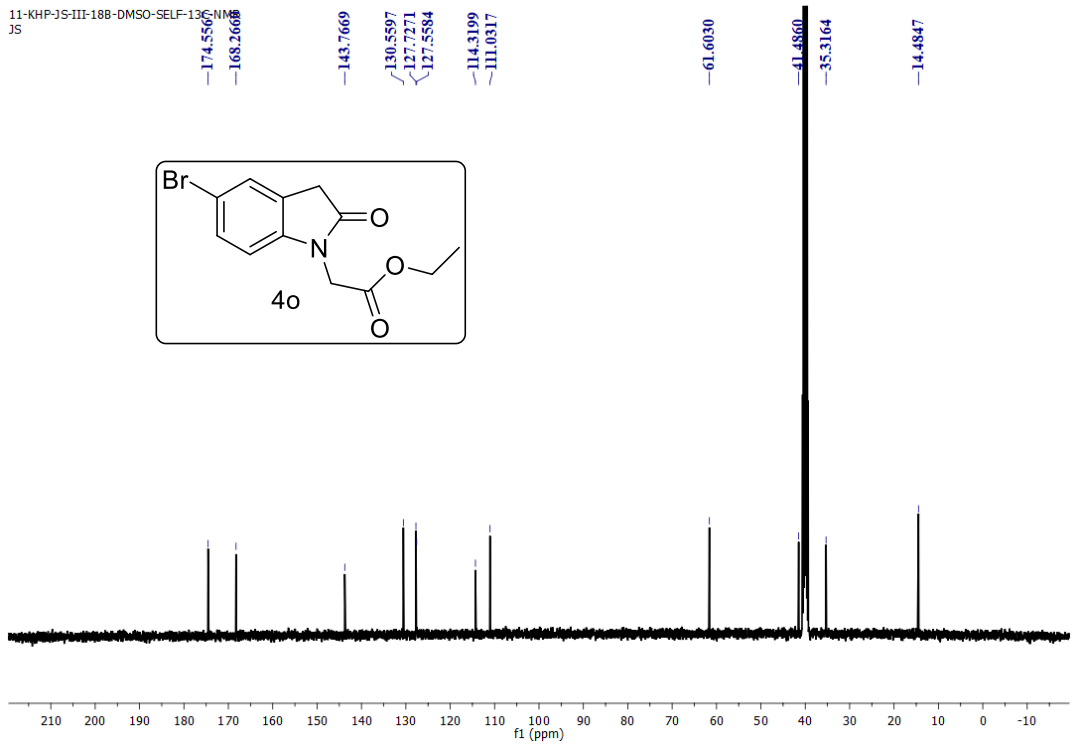
HRMS of 5-bromo-1-methylindolin-2-one(4n)



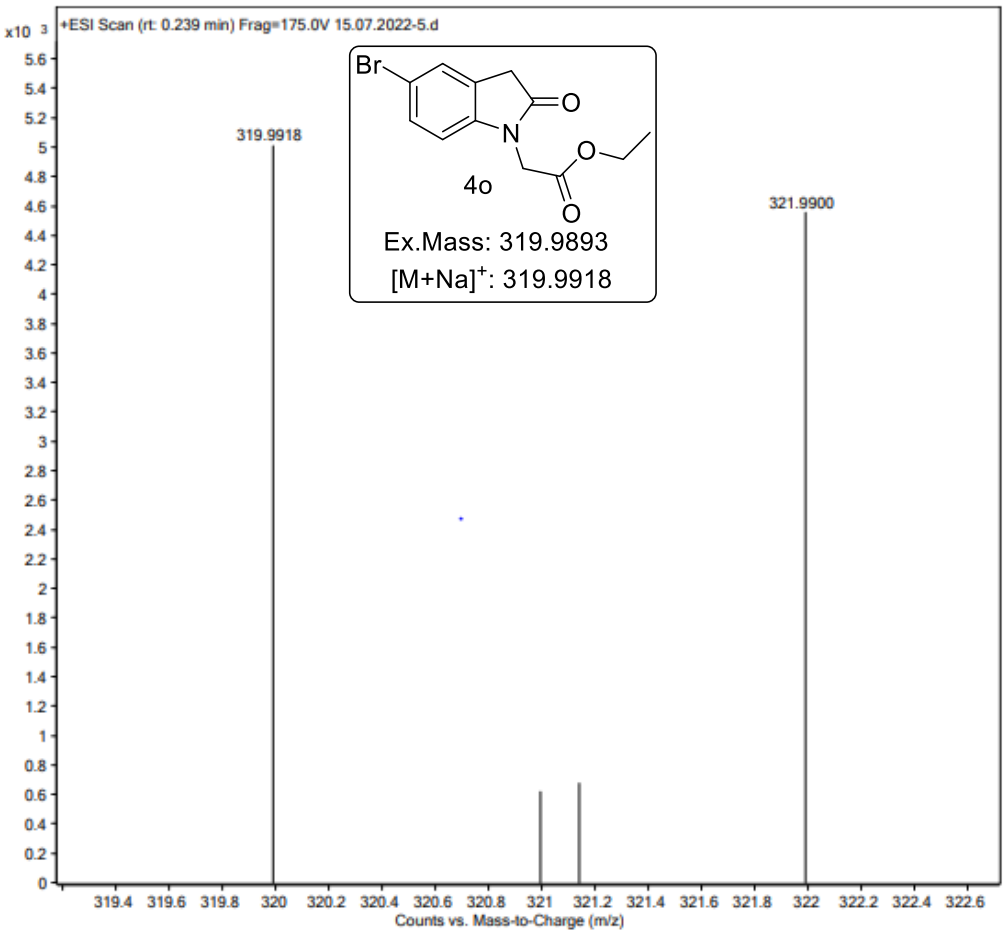
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of ethyl 2-(5-bromo-2-oxoindolin-1-yl)acetate (4o)



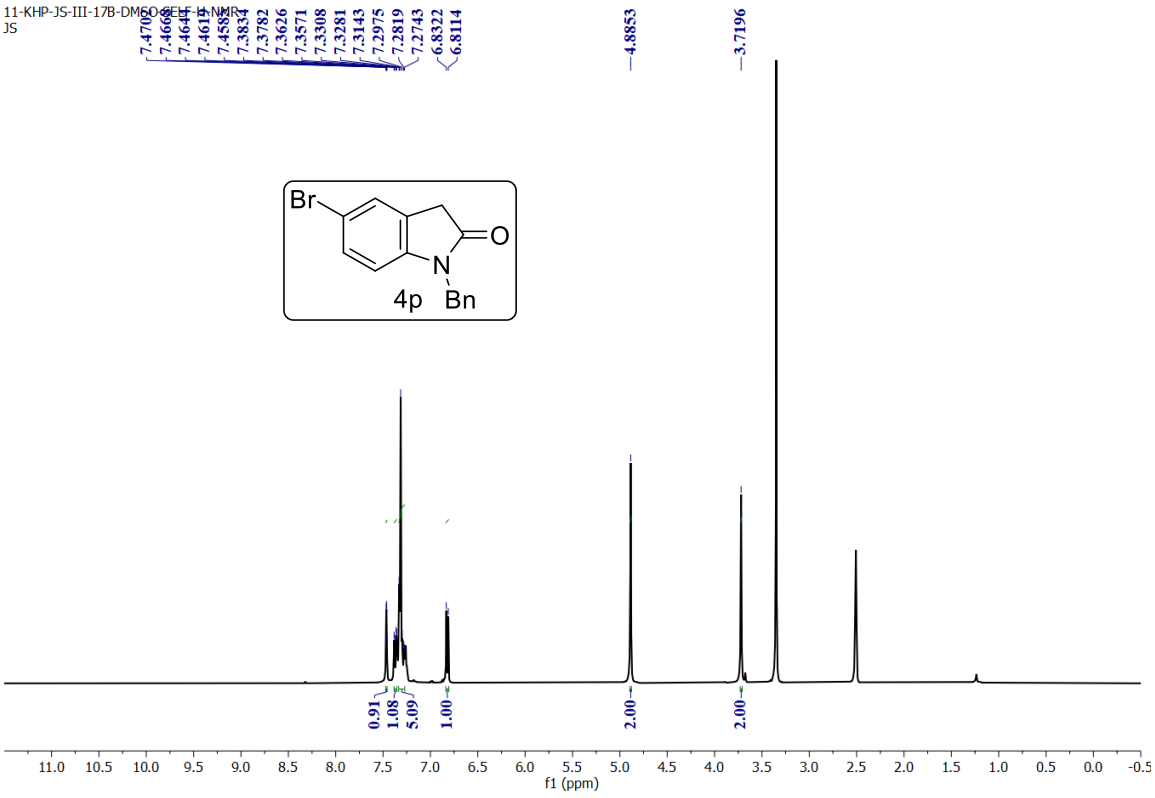
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of ethyl 2-(5-bromo-2-oxoindolin-1-yl)acetate (4o)



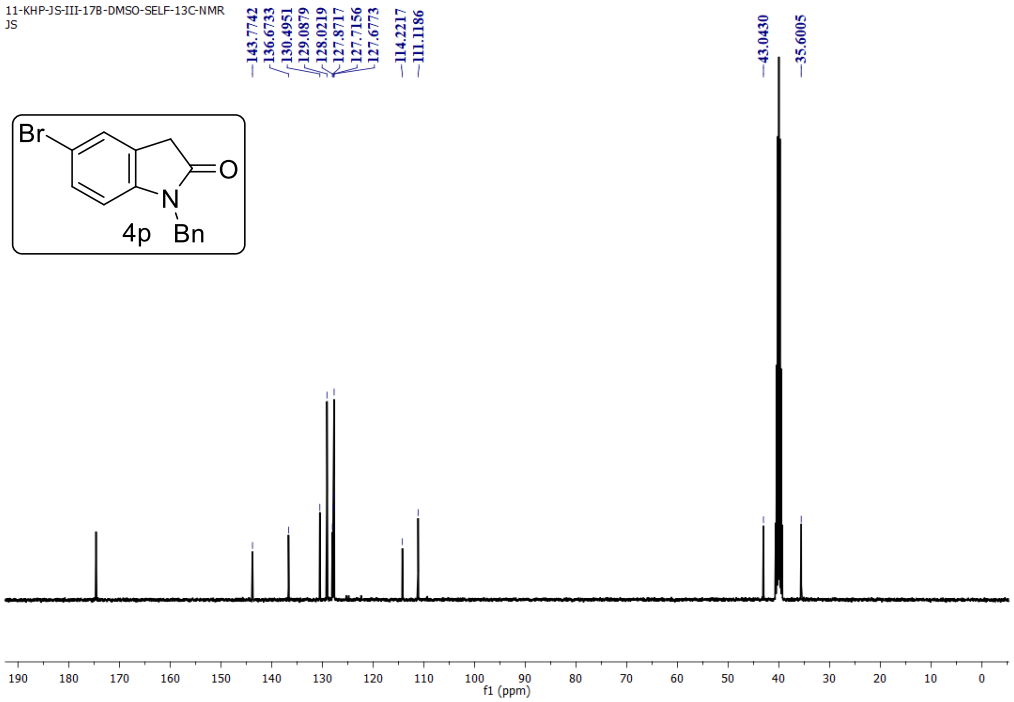
HRMS of ethyl 2-(5-bromo-2-oxoindolin-1-yl)acetate (4o)



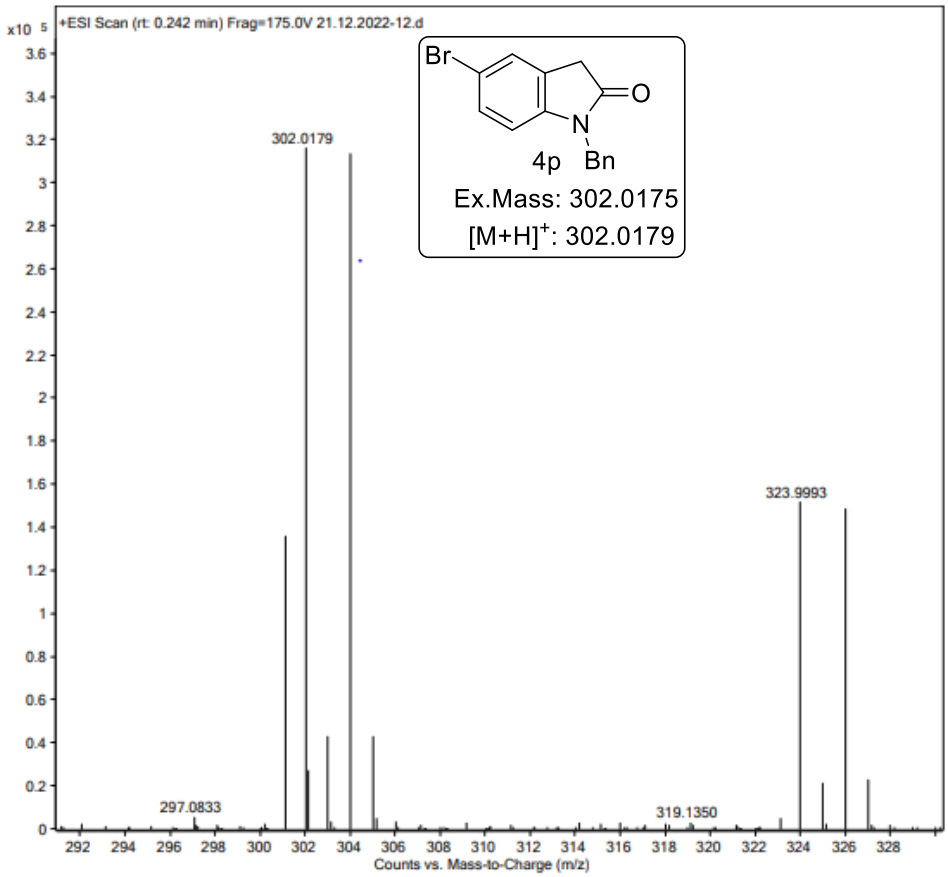
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 1-benzyl-5-bromoindolin-2-one (4p)



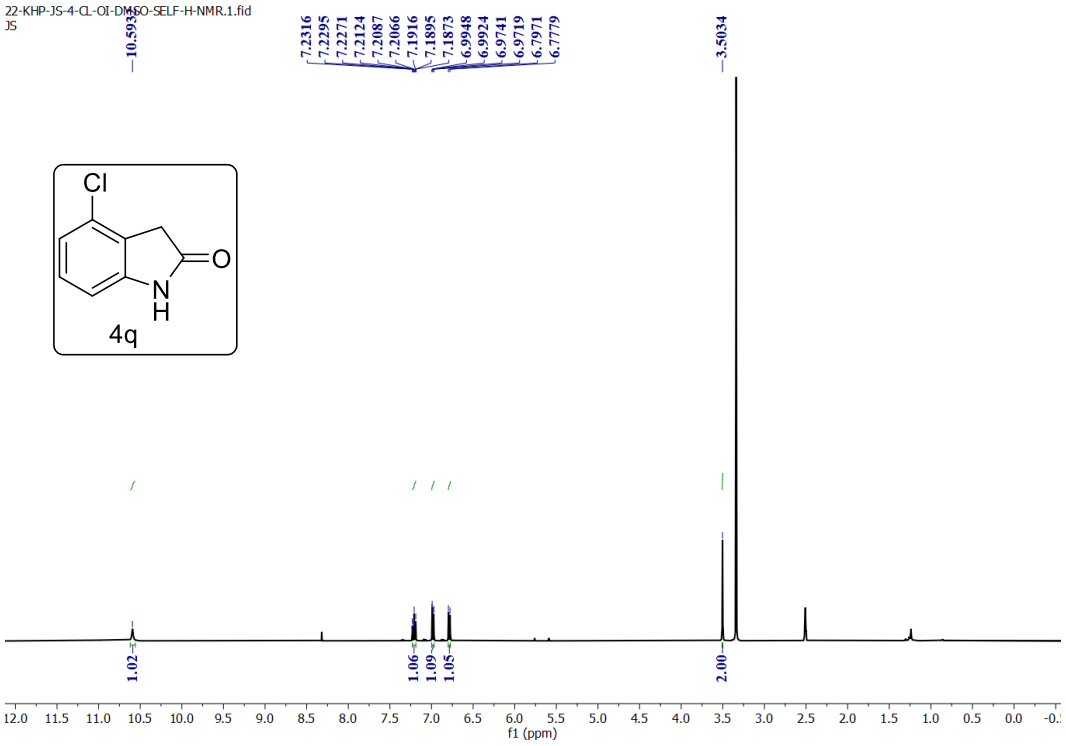
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of 1-benzyl-5-bromoindolin-2-one (4p)



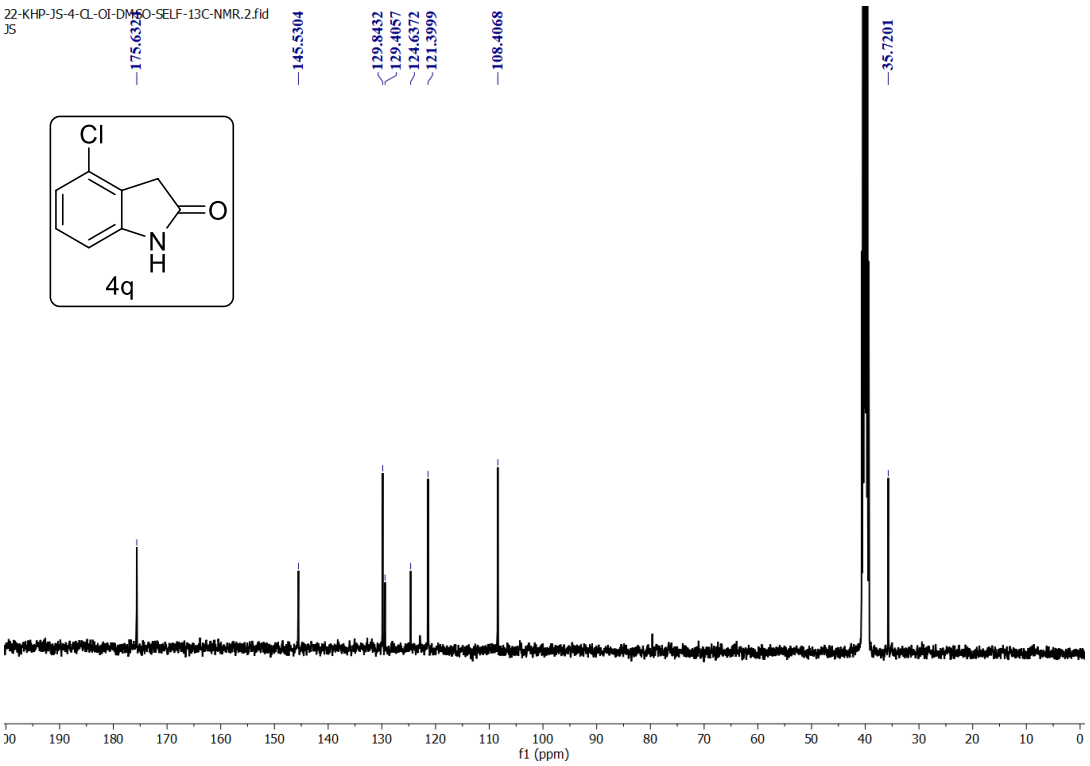
HRMS of 1-benzyl-5-bromoindolin-2-one (4p)



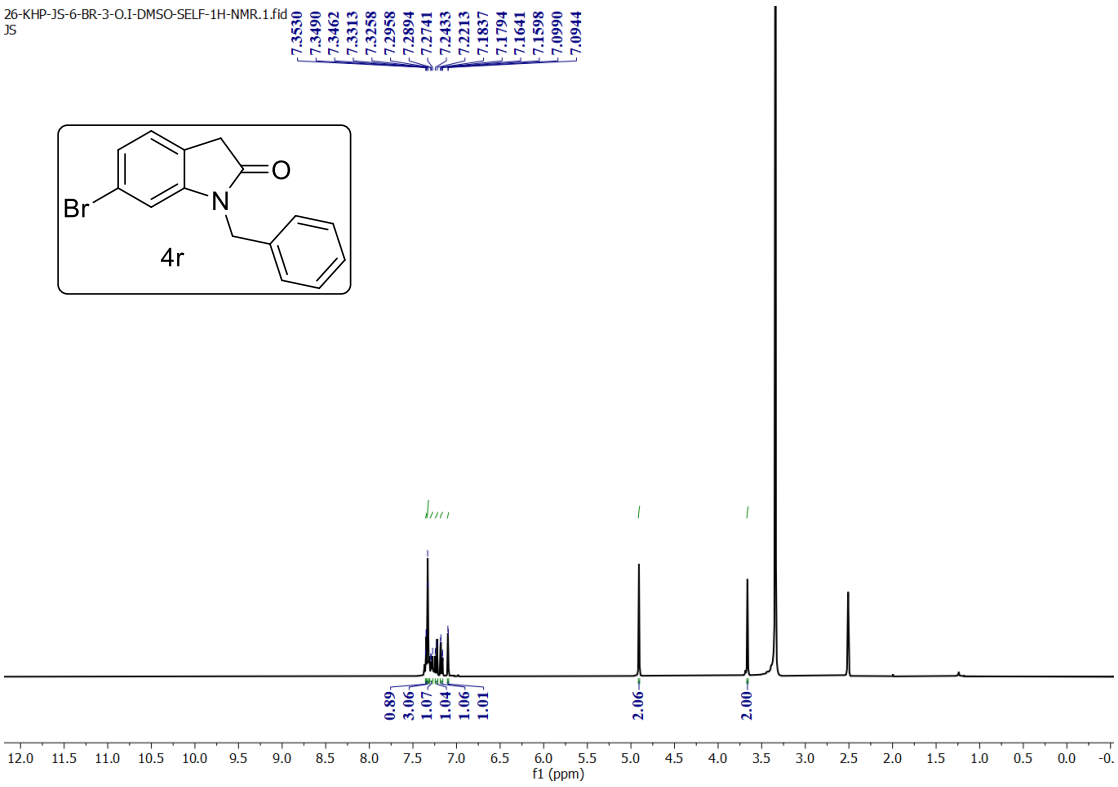
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 4-chloroindolin-2-one (4q)



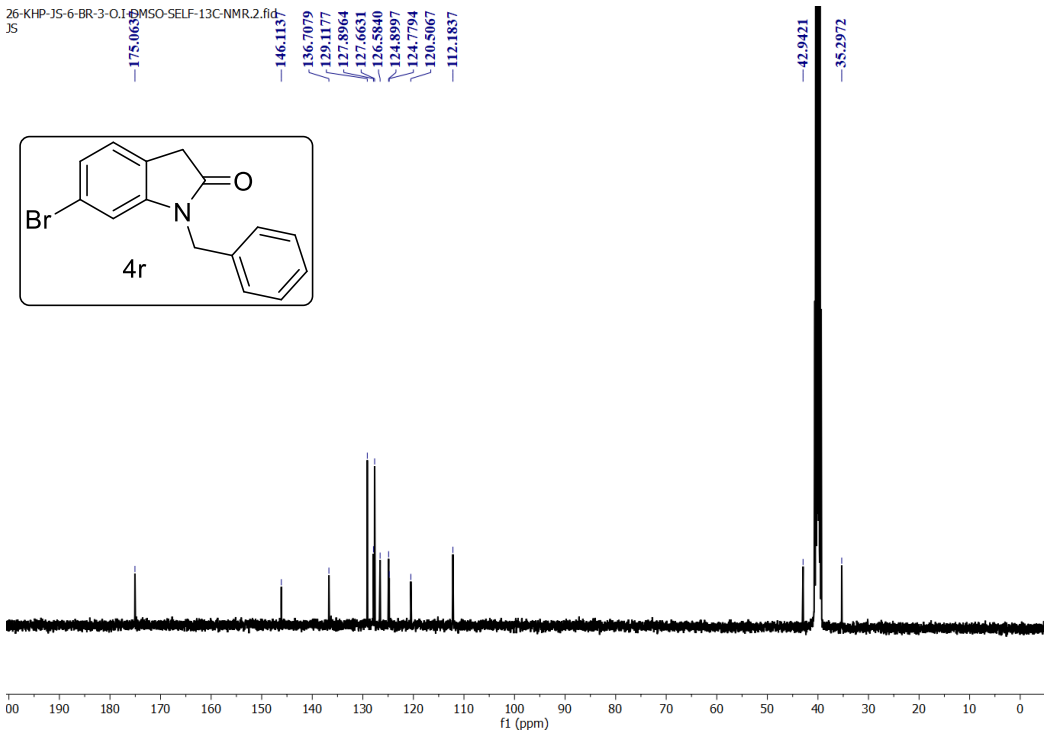
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of 4-chloroindolin-2-one (4q)



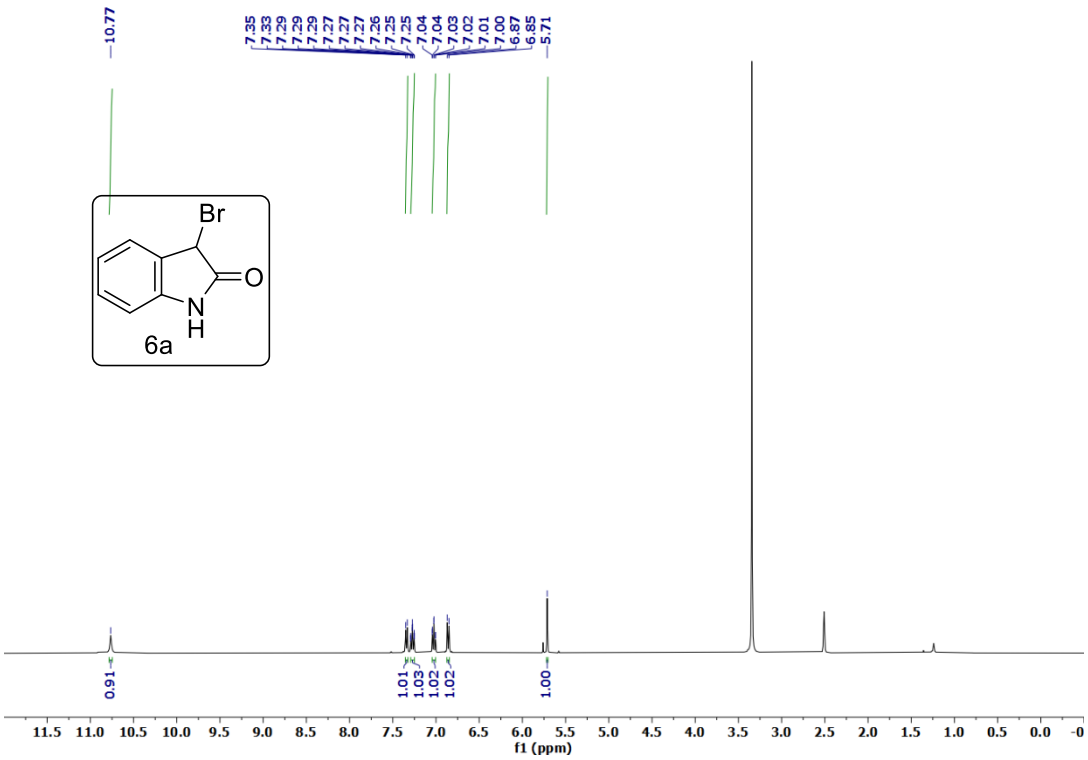
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 1-benzyl-6-bromoindolin-2-one (4r)



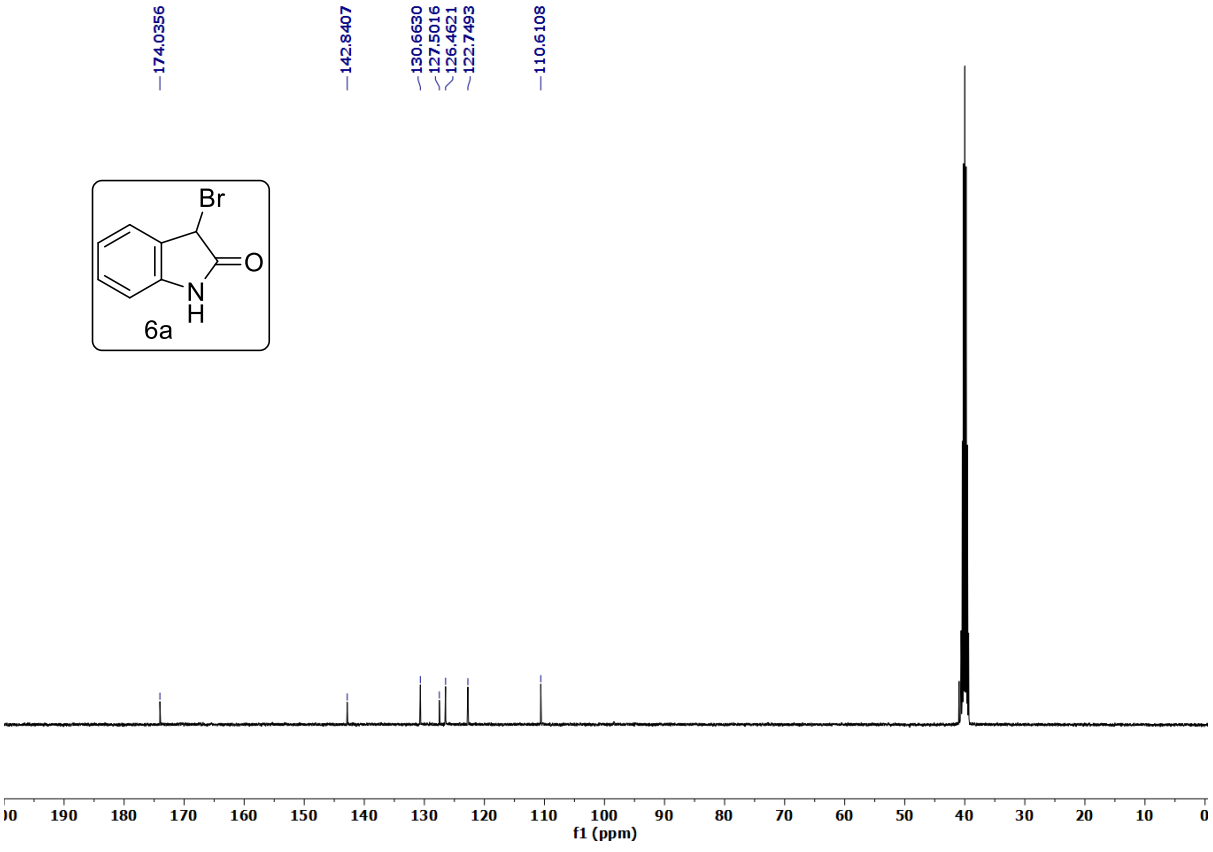
^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of 1-benzyl-6-bromoindolin-2-one (4r)



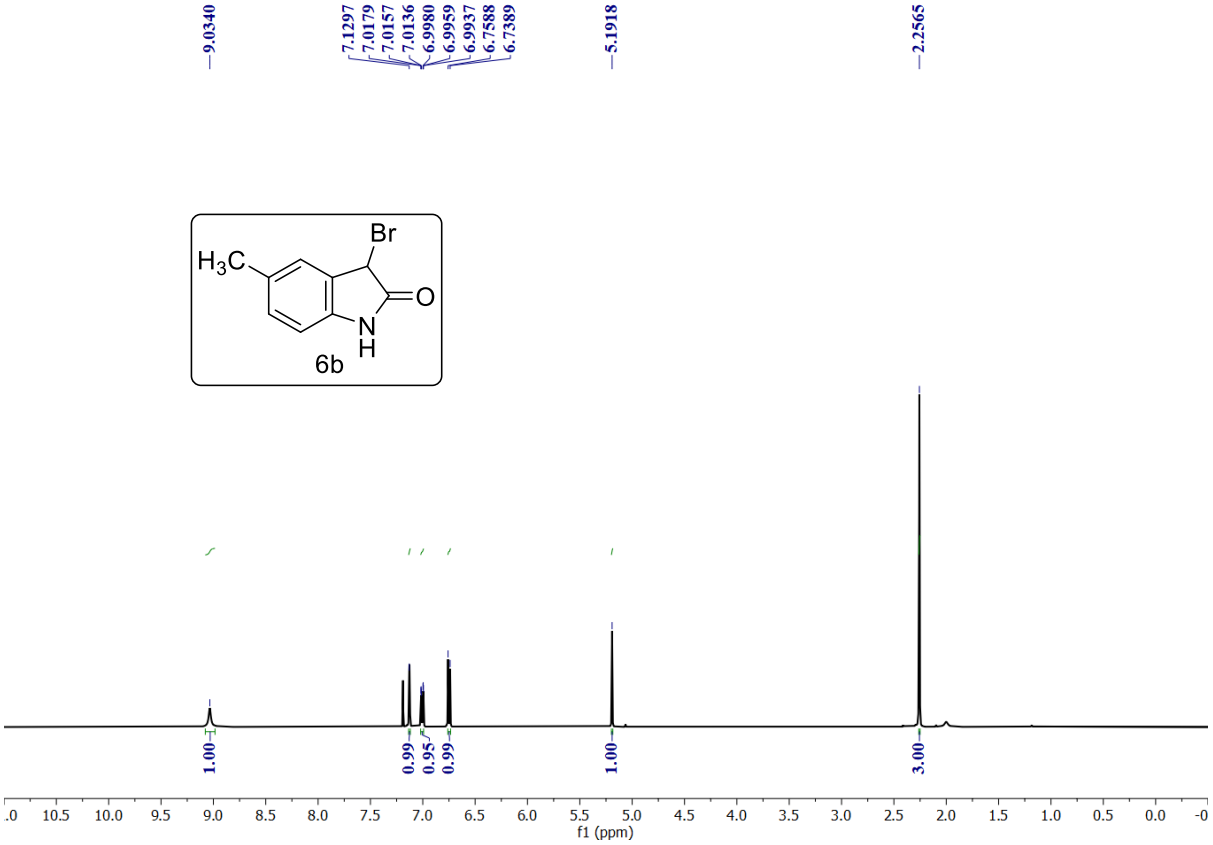
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-bromoindolin-2-one (6a)



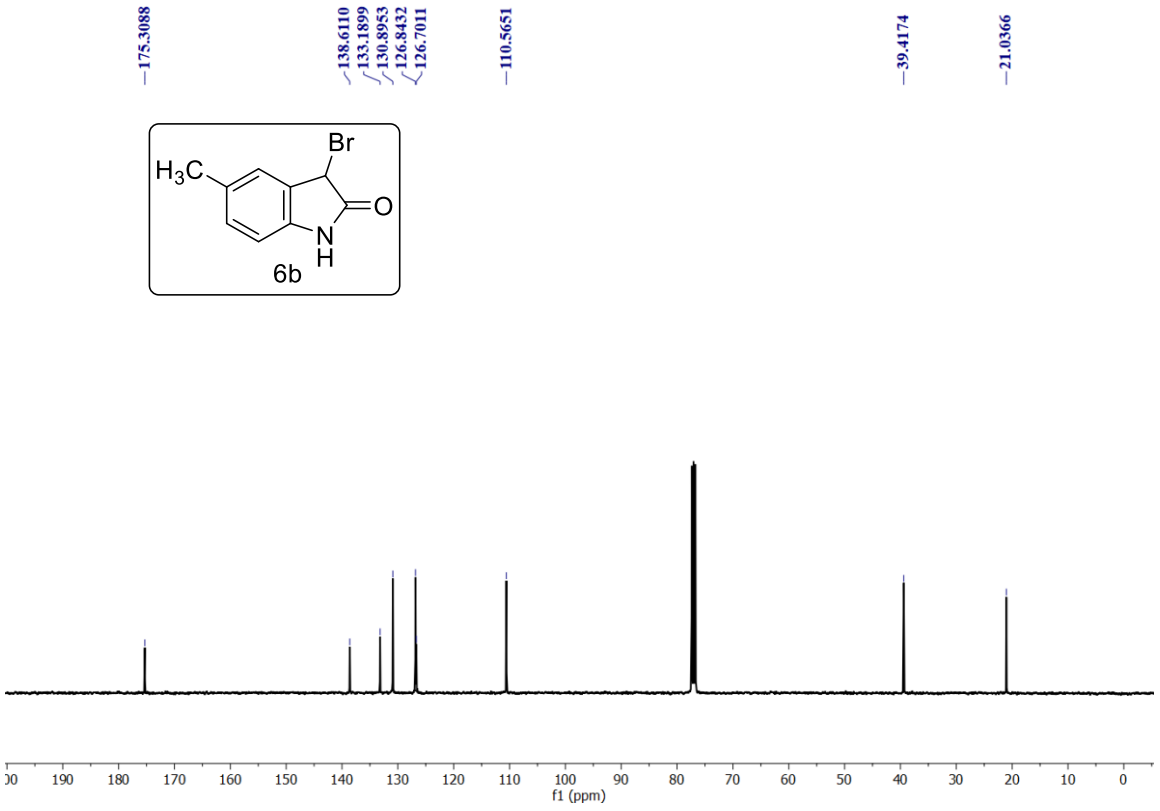
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of 3-bromoindolin-2-one (6a)



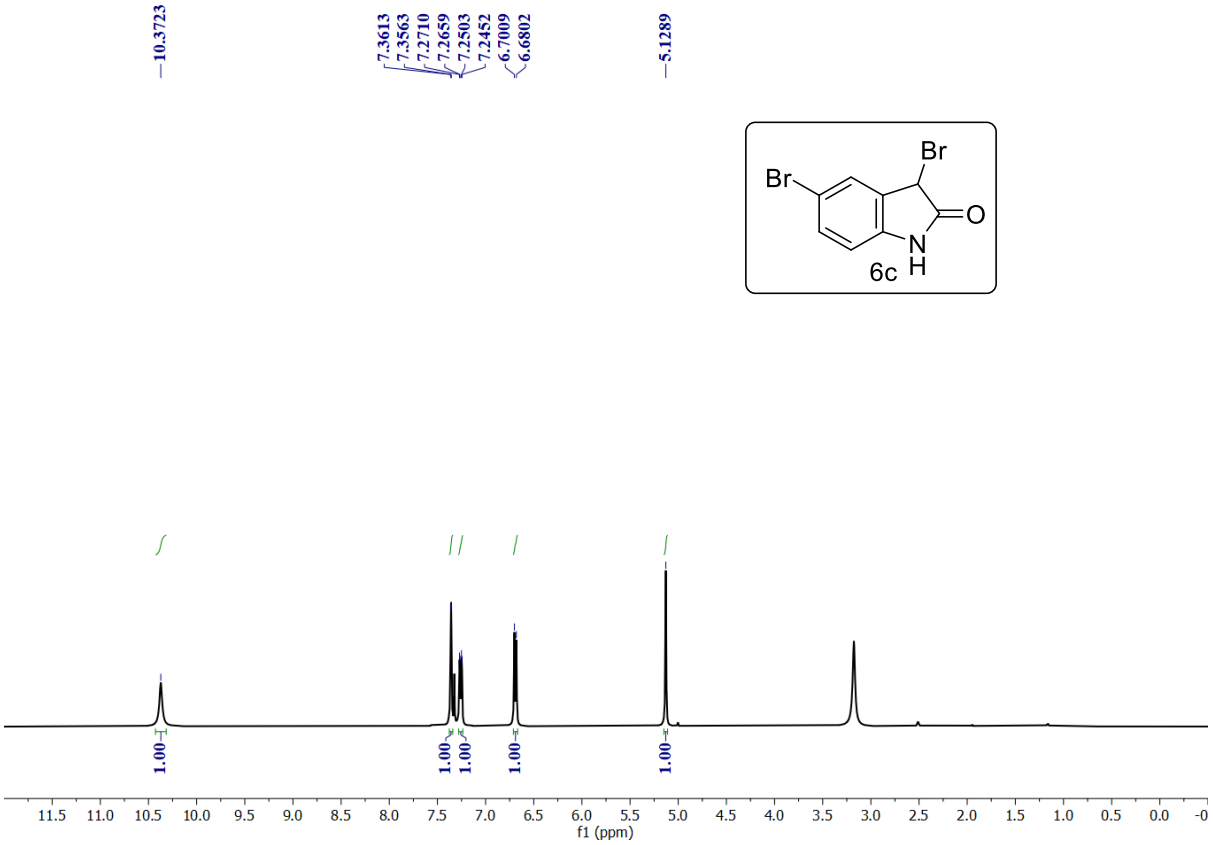
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-bromo-5-methylindolin-2-one (6b)



^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of 3-bromo-5-methylindolin-2-one (6b)



^{1}H NMR (400 MHz, $CDCl_3$+DMSO-d_6) spectrum of 3,5-dibromoindolin-2-one (6c)



^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$+DMSO-d_6) spectrum of 3,5-dibromoindolin-2-one (6c)